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KINETIC STUDIES ON THE CATIONIC POLYMERIZATION OF CYCLIC DIENES

SHINZO KOHJIYA

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CONTENTS

INTRODUCTION

Although the polymerization of cyclopentadiene was reported by Staudinger and Bruson[1] as early as in 1926, thereafter no academic studies had been published on the polymerization of cyclopentadiene or of other conjugated cyclic dienes till the 1950's. Staudinger and Bruson stated in their paper[1] that the rubbery polymer of cyclopentadiene was easily obtained with quite a large number of Friedel–Crafts catalysts.

In 1952, Wassermann et al.[2] reported the polymerization of cyclopentadiene by trichloroacetic acid and the formation of deeply coloured conducting polymer. However, the polymer had a low molecular weight and the polymerization mechanism was very complex. Thus this seemed to be a special case applicable only to cyclopentadiene.

In the 1960's, two Japanese schools started the investigation of the polymerization reaction of cyclic dienes. Aso et al.[3] studied the reactions and the polymer structures of cyclopentadiene and of substituted cyclopentadienes, while Yamaguchi et al.[4] investigated the reaction of cyclic dienes with sulfur dioxide and the formation of polysulfones. However, these studies focused their attention on the formation and the structures of the polymers.

A group of French researchers published a kinetic study[5] on the polymerization of cyclopentadiene by $TiCl_3$(O-n-Butyl) to

obtain a high molecular weight polycyclopentadiene, but they reported no quantitative results. Later they discussed mainly on the cocatalysis in ionic polymerization.[6] Some other reports have been published on the polymerization reaction of cyclic dienes, for example, on the polymerization of cyclohexadiene,[7,8] on the radiation-induced polymerization of cyclopentadiene,[9,10] though they did not deal with the general character of the polymerization of cyclic dienes.

Therefore, the reason of great reactivity of cyclopentadiene, observed by Staudinger and Bruson for the first time, has not been fully elucidated and the reactivities of conjugated cyclic dienes other than cyclopentadiene have remained almost unknown.

The mechanism of ionic polymerization, especially that of anionic one, has been extensively studied during the 1960's. In the field of anionic polymerization, the discovery of what is called a living polymer system was an important event. In this system no transfer or termination process takes place, so the kinetic treatment is much simplified. For example, the spectacular contribution of Szwarc et al.[11] revealed the mechanism of homogeneous anionic polymerization, and their studies clearly demonstrated the validity and the importance of kinetic study to elucidate the reaction mechanisms.

On the other hand, kinetic treatments have not been so successfully developed in the field of cationic polymerization as in the study of anionic one. The most principal reason was the difficulties to determine the rate constants of elementary

reactions.[12] This situation seemed to originate from the nature of the active species in cationic polymerization. Carbonium ions, which are reasonably assumed to be active species for the cationic polymerization, have not been successfully analyzed by spectroscopic or any other methods, because of their lack of stability. Thus, the kinetic studies in cationic polymerizations have encountered much difficulties in determining the concentration of active species which was necessary for evaluating the propagation rate constant. In addition, on account of the high reactivity of the carbonium ions, the kinetic features of cationic polymerization have often been complicated. Transfer and termination reactions take place persistently and a stationary state concentration of active species is not always attained. This was actually the case, for example, in the cationic polymerization of conjugated cyclic dienes.

In spite of these difficulties, there have been a few instances which successfully determined the propagation rate constant. They are the studies by Higashimura et al.[13] and those by Pepper et al.[14] The former is concerned with the propagation rate constant of the cationic polymerization in its stationary state. This made a large contribution to clarify the mechanism of the cationic polymerization in stationary state. Regrettably, not a few polymerization systems were found to be non-stationary in cationic polymerization. For this reason, the method developed by Higashimura et al. has been applied only to the iodine catalysis but not to non-stationary state polymerization induced by a number of Friedel–Crafts halides. The latter is concerned with a typical

example of non-stationary state polymerization. Pepper studied the polymerization of styrene by sulfuric acid, and found that the initiation reaction was very rapid and the concentration of active species decreased during the polymerization as a result of some termination reactions. Assuming a unimolecular termination reaction, Pepper derived the rate equations and calculated the rate constants in the polymerization of styrene by sulfuric acid.[15] This method is, however, mainly applicable to strong mineral acid catalysts, and it is desirable to find a method covering widespread Friedel–Crafts halides.

With these backgrounds, the author started the kinetic studies on the cationic polymerization of cyclic dienes with two purposes.

One is to clarify the high reactivity of conjugated cyclic dienes, which has sometimes been referred to by several authors in relation to their structures. For this purpose, the cationic polymerization of conjugated cyclic dienes with 5 to 8 ring carbon atoms, the copolymerization with vinyl monomers, and the copolymerization between cyclic dienes were investigated. Through these studies, the relation between the reactivity and the monomer structure was expected to become clear.

The other is to examine the possibility of evaluating the rate constants of elementary reactions in cationic polymerization. The rate constant could be a direct measure of the reactivity, so the reason for the high reactivity of conjugated cyclic dienes is expected to be clarified. Furthermore, the determination of the

propagation rate constant would make a far-reaching contribution to the kinetic study of cationic polymerization. Cyclopentadiene seemed to be especially promising for this purpose, because the polymerization of this monomer by $TiCl_4$ showed kinetic behaviours similar to those of styrene-H_2SO_4 system, which was suggested by Momiyama et al.[16] The author accomplished the kinetic scheme to interpret the kinetic behaviours of conjugated cyclic dienes. This scheme is in some way the extension of the non-stationary state kinetics proposed by Pepper et al. The author also designed the experimental apparatus which enabled him to conduct the reaction under a rigourous condition and to measure accurately the large rate of polymerization.

Bearing these two purposes in mind, which are advantageously amalgamated in the study of the reactivity of cyclic dienes, a systematic study has been carried out as following.

In the first part, cationic polymerizations of four conjugated cyclic dienes were studied. All the dienes studied were found to be very reactive in cationic polymerization. In addition, the majority of the polymerization systems was found to be kinetically non-stationary i.e. a stationary concentration of active species was not attained during the polymerization and resulted in non-linearity of the first-order plot of the monomer consumption. Concerning cyclopentadiene and methylcyclopentadiene, which were the most reactive among cyclic dienes studied, the polymerizations were non-stationary with many kinds of catalysts. For the other dienes, when a weak Lewis acid such as

boron trifloride etherate was used, the polymerization was a stationary one. From these studies, the importance of the combination of monomer and catalyst was shown in the cationic polymerization of cyclic dienes to establish a stationary state polymerization. The choice of a different monomer or of a different catalyst induced the change not only of the rate or of the degree of polymerization, but also of the kinetic behaviour (stationary or non-stationary). Combinations of reactive monomers and strong catalysts always resulted in a non-stationary state polymerization, and in this case the propagation rate constant was determined by the appropriate kinetic treatment, which is described in Part III (see below).

The copolymerization studies are described in Part II to investigate the relation between the reactivity and the structure of monomers. Cyclopentadiene was copolymerized with α-methylstyrene and with 2-chloroethyl vinyl ether. It was found that cyclopentadiene was more reactive than α-methylstyrene and as reactive as 2-chloroethyl vinyl ether. Some physical properties of the copolymers were also investigated. In reference to the results published previously,[17] the nucleophilicity of monomers and the stability of carbonium ions are proposed for the factors determining the monomer reactivity. Contributions of these factors were discussed on the basis of the solvent effect in the cationic copolymerizations.

Copolymerizations between cyclic dienes were also carried out. The reactivity was found to decrease as the ring size increases.

Thus the reactivity order is:

Methylcyclopentadiene > Cyclopentadiene > 1,3-Cyclohexadiene > 1,3-Cycloheptadiene > 1,3-Cycloöctadiene.

This order is in accordance with the results in the homopolymerization of these monomers.

In Part III, the propagation rate constant of cyclopentadiene were determined according to the treatment by non-stationary state kinetics. The propagation rate constant of the polymerization initiated by $TiCl_4$-trichloroacetic acid in toluene at -75°C was 350 l/mole/sec. This is very large for the propagating carbonium ion presumably existed as an ion-pair form. Indeed this is the largest propagation rate constant so far reported for the ion-pair species.

The propagation rate constant of the polymerization initiated by perchloric acid was nearly equal to that by acetyl perchlorate, which was reasonably explained by the identity of the counter ion (ClO_4^-). This gave a support for the validity of the present kinetic treatment.

To clarify what is responsible for the large propagation rate constant, activation energy and frequency factor were determined. At elevated temperatures, the rate constants became much larger and the activation energy was determined to be 6.0 Kcal/mole and log of frequency factor was 10. Only a few data are available for activation parameters of the propagation reaction in cationic polymerizations, so the extensive discussion on these values are

not possible at present. At least it is certain that the large rate constant is mainly due to the entropy factor. It might be proposed that in the cationic polymerization of cyclic dienes an entropy term is responsible for their high reactivity. Undoubtedly more experiments are needed for this proposition to be firm.

To summarize, conjugated cyclic dienes were found to be highly reactive in cationic polymerizations, and the kinetic investigations of these monomers, especially of cyclopentadiene, elucidated the reason of the high reactivity of cyclic dienes and the mechanism of the cationic polymerization in its non-stationary state.

The author hopes that this study will make some contribution to the chemistry and the kinetic study of the cationic polymerizations.

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PART I

POLYMERIZATION REACTION OF CYCLIC DIENES WITH CATIONIC CATALYSTS

Chapter 1

Cyclopentadiene

In the 1920's Staudinger and Bruson[1] studied the polymerization of cyclopentadiene (CPD) with a number of metal halides and found that CPD was polymerized to a rubbery polymer under some selected conditions. Since then some investigations have been carried out on the polymerization of CPD, but little have been made on the polymerization mechanism of CPD.

Momiyama et al.[2] studied the polymerization of CPD by several Friedel-Crafts halides and suggested that the reactivity of CPD was very large in the cationic polymerization, and that the peculiar kinetic features were observed in the polymerization with titanium tetrachloride-trichloroacetic acid.

In this chapter, the polymerizations of CPD by titanium tetrachloride-trichloroacetic acid, stannic chloride-trichloroacetic acid, and boron trifluoride etherate were studied. The kinetic features of these systems are described and a few rate constant ratios are reported.

Section 1.1

Polymerization with Titanium Tetrachloride-Trichloroacetic Acid

INTRODUCTION

The polymerization of CPD with $TiCl_4$-CCl_3COOH at a low temperature was found to proceed very rapidly at an initial stage but immediately reach a final yield though some monomers remain unreached (the saturation of the conversion).[2] Analogous behaviours have been observed in several systems.[3),4)] Pepper derived the kinetic equations for styrene-sulfuric acid system, which enabled him to interpret the experimental results quantitatively and to evaluate rate constants of elementary reactions. The present study was undertaken to clarify the reasons for the saturation phenomena of the conversion and to calculate the rate constant ratios by applying the Pepper type kinetic treatment.

EXPERIMENTAL

Materials

Cyclopentadiene (CPD) CPD was obtained by the pyrolysis of dicyclopentadiene. Dicyclopentadiene was washed with aqueous potassium carbonate solution, water, dilute hydrochloric acid, and finally water, dried overnight with anhydrous sodium sulfate,

and distilled twice under reduced pressure. Dicyclopentadiene thus purified was pyrolyzed according to the reported method.[5] CPD was collected and stored at -78°C, and again distilled from calcium hydride just before use (b.p. 40 — 41°C).

Catalysts $TiCl_4$ was distilled into small glass ampoules. Commercial trichloroacetic acid (TCA, guaranteed reagent) was used without further purification. The equimolar mixture of $TiCl_4$ and TCA was used to start the polymerization, unless otherwise stated.

Toluene Toluene was washed with sulfuric acid, water, aqueous sodium hydroxide solution, and finally water, dried over calcium chloride, refluxed on calcium hydride overnight, and distilled. It was again refluxed and distilled over calcium hydride just before use.

Procedures

Polymerizations were carried out in an all glass apparatus submerged in a dry ice–methanol bath. The polymerization flask was equipped with a monomer inlet, an outlet, and a magnetic stirrer. Toluene and catalyst solution were introduced into the apparatus. After thermal equilibration, a known amount of precooled monomer was added to the flask with a syringe through the self-sealing rubber cap of the inlet. The polymerization was started under a vigorous agitation. After suitable time intervals, an aliquot amount of the polymerizing solution was withdrawn through the self-sealing rubber cap of the outlet with a syringe and discharged into a large amount of methanol to stop the

polymerization.

The polymer precipitate was washed repeatedly with methanol, dried in vacuo, and weighed. Methanol employed in the present study contained a small amount of 4,4'-thiobis-(6-t-butyl-3-methylphenol) as an antioxidant.

Molecular weights of the polymers were compared in terms of the intrinsic viscosity of the benzene solution at 30°C.

Water contents of the reagents and of the polymerization systems were determined by the Karl Fischer method.

RESULTS

1. Effects of Various Reagents on the Saturation of Conversion.

Polymerizations were carried out at monomer concentration of 1.2 mole/l at -78°C by $TiCl_4$-TCA. Under these conditions, the polymerization rapidly proceeded and within a minute reached a final yield having a part of the monomer unreacted. This phenomenon is explained either by the rapid thermodynamic equilibration between the polymer and the monomer or by the consumption of a reagent necessary to sustain the polymerization.

Figure 1 shows the absence of the effect of the additional monomer, which eliminates the possibility of the thermodynamic equilibration as a reason for the saturation phenomenon. Figures 2, 3 and 4 depict the effect of the addition of TCA, $TiCl_4$-TCA, and $TiCl_4$, respectively. These results clearly indicate that $TiCl_4$ was consumed during the polymerization, and the consumption of $TiCl_4$ caused the saturation of the conversion. Thus the addition

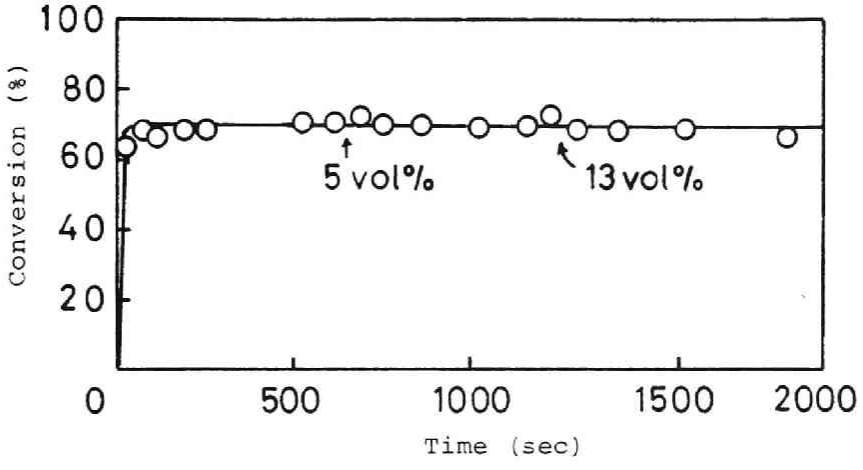


Fig. 1. Effect of addition of monomer on the dormant polymerization system. $[M]_o$ 1.2 mole/l (10 vol%), [C] 3.0 mmole/l, Solvent toluene, -78°C.

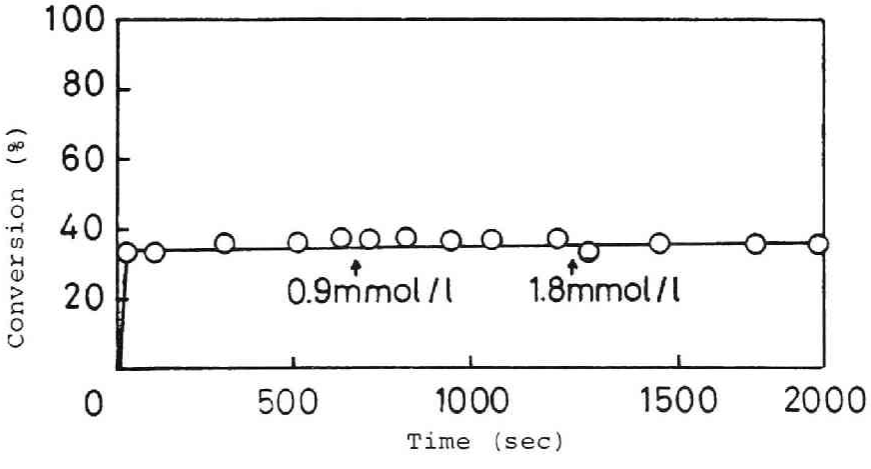


Fig. 2. Effect of addition of trichloroacetic acid on the dormant polymerization system. $[M]_o$ 1.2 mole/l, [C] 1.0 mmole/l, Solvent toluene, -78°C.

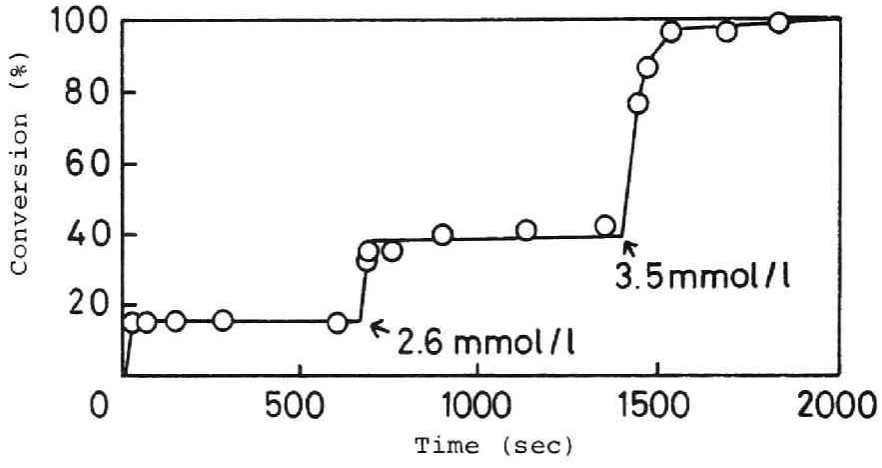


Fig. 3. Effect of addition of $TiCl_4$-CCl_3CO_2H on the dormant polymerization system. $[M]_o$ 1.2 mole/l, [C] 1.0 mmole/l, Solvent toluene, -78°C.

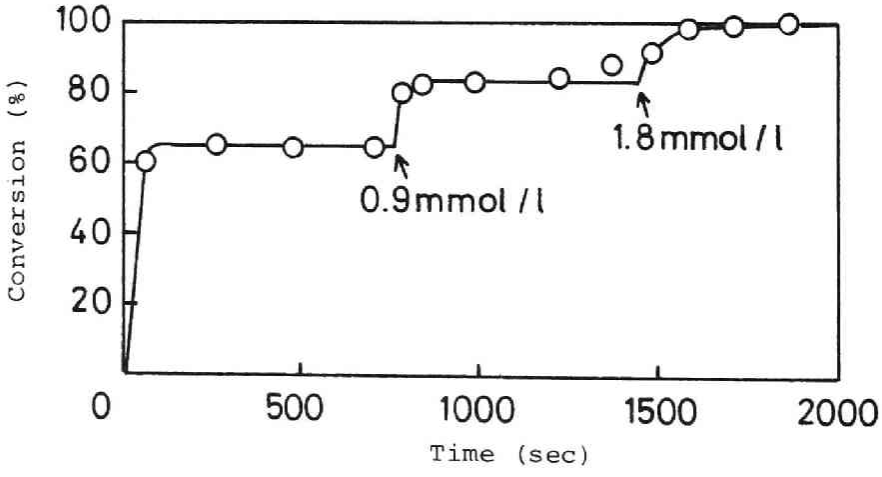


Fig. 4. Effect of addition of $TiCl_4$ on the dormant polymerization system. $[M]_o$ 1.2 mole/l, [C] 2.0 mmole/l, Solvent toluene, -78°C.

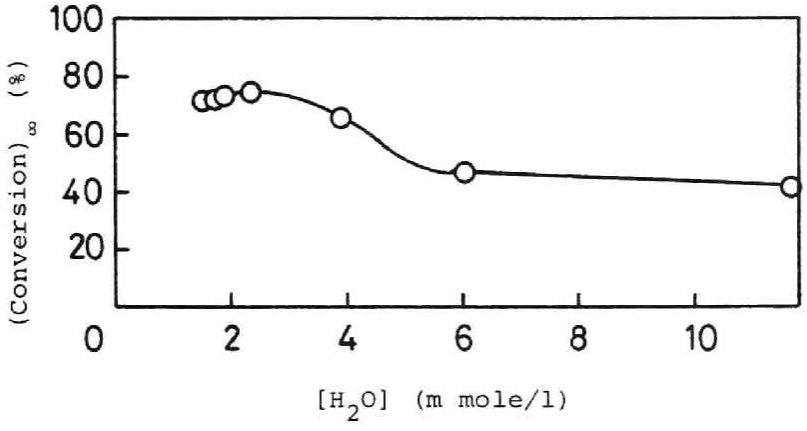


Fig. 5. Effect of water concentration on the final conversion. $[M]_o$ 1.2 mole/l, [C] 2.0 mmole/l, Solvent toluene, -78°C.

of $TiCl_4$ on the dormant system reinitiated the polymerization as shown in Figure 4. The intrinsic viscosity of the polymer was not changed with the addition of monomer or TCA, while the annexing of $TiCl_4$-TCA or $TiCl_4$ decreased the polymer viscosity a little. From these results, it is clear that the saturation of the conversion is caused by the consumption of $TiCl_4$.

2. Effects of the Concentration of the Reagents on the Final Yield.

The results in the previous subsection showed a poor reproducibility of the final yield, probably because of the difference in the residual water content of the polymerization system. In fact, the water content of the system strongly affected the final yield

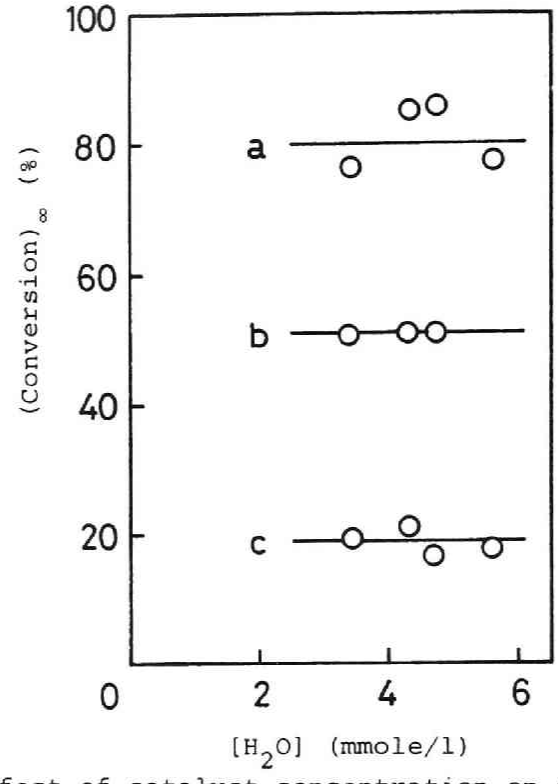


Fig. 6. Effect of catalyst concentration on the final conversion. $[M]_o$ 1.2 mole/l, Solvent toluene, -78°C, $[C]_o$ (mmole/l) a 3.0, b 2.0, c 1.0.

as indicated in Figure 5. The water content exceeding 5 mmole/l did not change the yield, which seemed to be due to the poor solubility of water in toluene at low temperatures. The polymer molecular weight was not much affected and intrinsic viscosity ranged from 0.15 to 0.18 under the conditions shown in Figure 5.

The effect of the catalyst concentration on the final yield and on the intrinsic viscosity of the polymer are shown in Figures 6 and 7. An increase in catalyst concentration increased the final yield, but decreased the molecular weight of polymer.

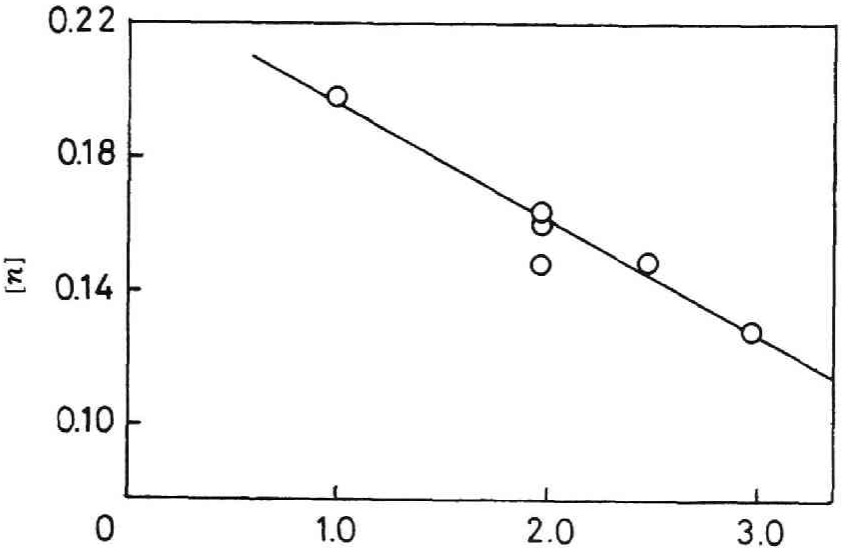


Fig. 7. Effect of catalyst concentration on [η] of polymer. Polymerization conditions are the same as in Fig. 6.

Similar effects were observed when the concentration of trichloroacetic acid was changed as shown in Figures 8 and 9. An increase of TCA concentration relative to $TiCl_4$ had apparently the same effects as that of catalyst concentration.

The change of the monomer concentration showed an interesting phenomenon. The higher the initial monomer concentration, the lower the final yield though the weight of the polymer increased with the increase of the monomer concentration. The results are shown in Figure 10. However, the higher the monomer concentration,

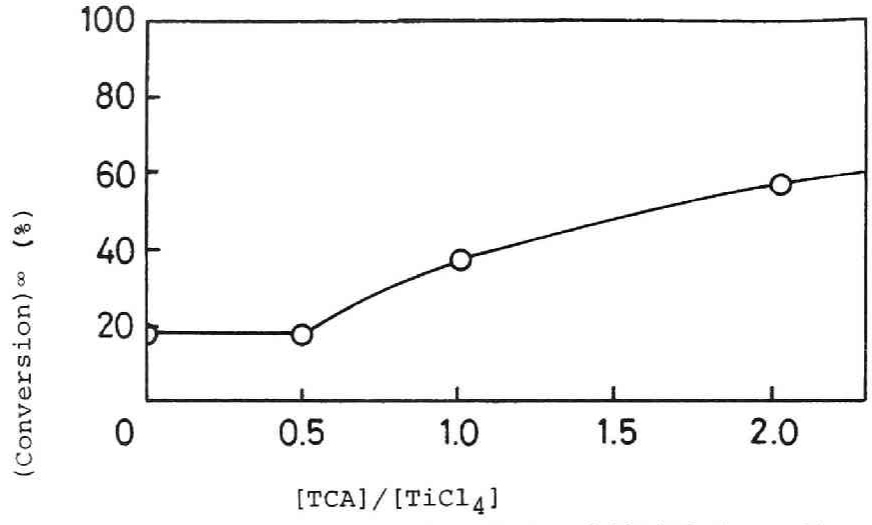


Fig. 8. Effect of mole ratio of [TCA]/[$TiCl_4$] on the final conversion. $[M]_o$ 1.2 mole/l, [$TiCl_4$] 1.5 mmole/l, [H_2O] 2.5 mmole/l, Solvent toluene, -78°C.

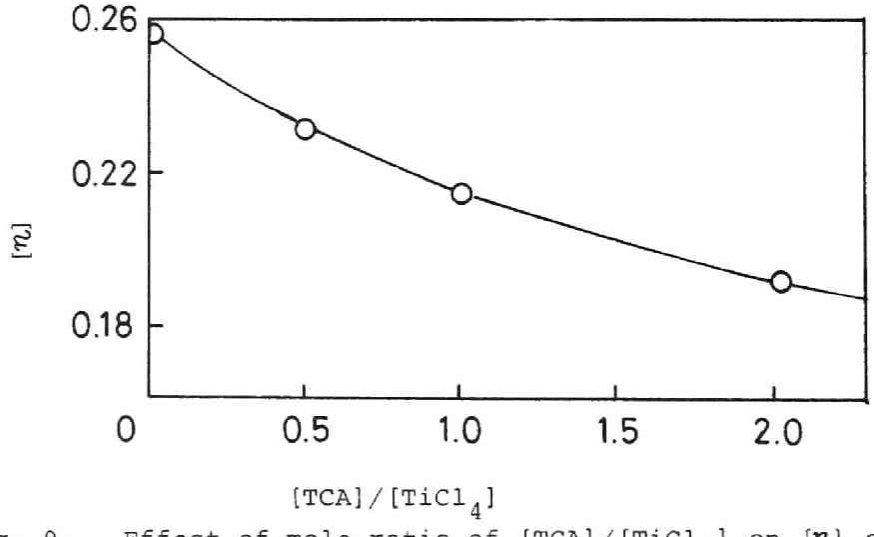


Fig. 9. Effect of mole ratio of [TCA]/[$TiCl_4$] on [η] of polymer. Polymerization conditions are the same as in Fig.8.

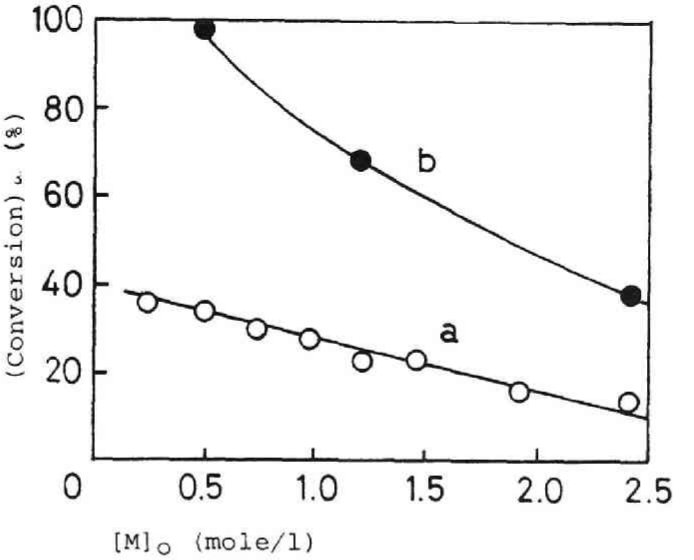


Fig. 10. Effect of monomer concentration on the final conversion. Solvent toluene, -78°C,
a (○) [C] 1.0 mmole/l, [H_2O] 3.8 mmole/l,
b (●) [C] 2.0 mmole/l, [H_2O] 1.6 mmole/l.

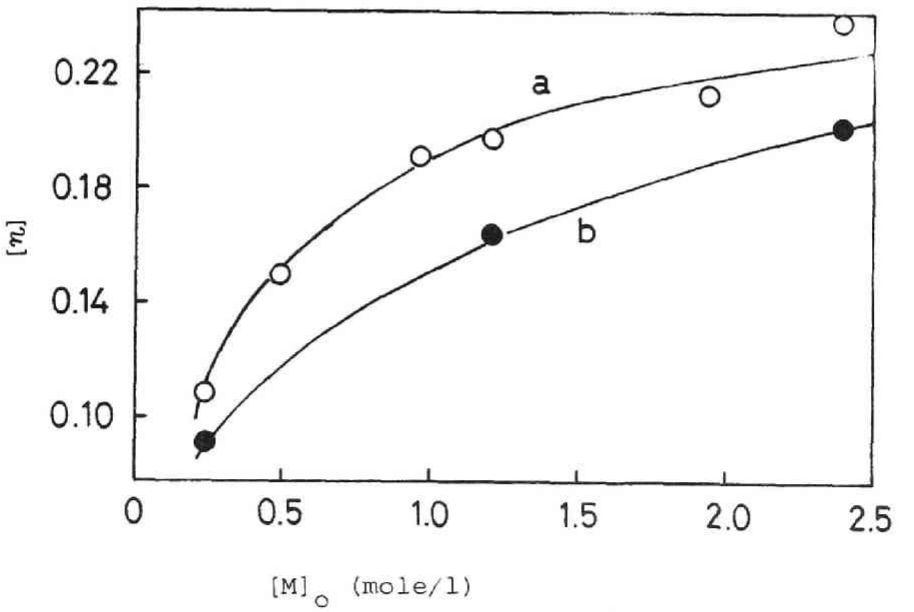


Fig. 11. Effect of monomer concentration on $[\eta]$ of polymer. Polymerization conditions and marks are the same as in Fig. 10.

the higher the molecular weight as shown in Figure 11.

DISCUSSION

The polymerization of CPD by $TiCl_4$-TCA proceeded very rapidly and reached final yield within a minute. The addition of CPD or TCA on the dormant system had no effect, but the addition of $TiCl_4$-TCA or $TiCl_4$ reinitiated the polymerization and consumed the residual monomer. Therefore it is concluded that the consumption of $TiCl_4$ is the reason for the saturation of the conversion.

As was already stated, the saturation phenomenon was also observed in the polymerization of styrene by sulfuric acid.[4] A very large rate was noted and this was ascribed to a rapid initiation i.e. an immediate consumption of sulfuric acid.

Pepper et al. proposed the following elementary reactions:

$$C + M \longrightarrow M^* \ (=P_1^*) \qquad k_1 \qquad (1)$$

$$P_n^* + M \longrightarrow P_{n+1}^* \qquad k_2 \qquad (2)$$

$$P_x^* \longrightarrow P_x + C \qquad k_3 \qquad (3)$$

$$P_x^* + M \longrightarrow P_x + M^* \qquad k_4 \qquad (4)$$

$$P_x^* \longrightarrow P_x \qquad k_5 \qquad (5)$$

where C denotes the catalyst, P^* is a propagating species, and n and x denote the degree of polymerization.

Assuming a rapid initiation i.e. $k_1 \gg k_2, k_3, k_4, k_5$, Pepper derived the following equations:

$$Y = 1 - \frac{M_\infty}{M_o} = 1 - \exp\left\{\left(-\frac{k_2}{k_5}\right)C_o\right\} \qquad (6)$$

$$\frac{1}{\overline{P}_n} = \frac{k_4}{k_2} + \frac{k_3 + k_5}{k_5} \cdot \frac{C_o}{M_o - M_\infty} \qquad (7)$$

where M_o denotes the initial monomer concentration, and M_∞ the monomer concentration at an infinite time when the final yield is attained.

According to the equation (6), the final yield Y is a function of $(-k_2/k_5) \cdot C_o$ and independent of M_o. This is different from the results shown in Figure 10. In the present system, the final yield was a function of the initial monomer concentration. There appear to be two possible explanations of this relation:

(a) The excess monomer may form an inactive complex with $TiCl_4$, which competes with the initiation.

(b) The monomer or the produced polymer may react with the propagating species to terminate growth.

A termination of the growing species by the excess monomer (higher than first order with reference to [M]) is less likely so long as a long polymer chain is produced. So, if any termination reaction is responsible for this event, a reaction of the growing species with the double bonds in the polymer seems more likely. However, the presence of cyclopentene or cyclohexene did not affect the polymerization at all.[6] Thus a termination reaction involving a polymer is also unlikely.

It is well-known that CPD forms a peculiar sandwich type complex with metals, for example, titanocene (biscyclopentadienyl titanium dichloride). This reaction is quite attractive as candidate for the above (a). From this consideration, the following

reaction is added to a series of elementary reactions (1)-(5):

$$C + 2M \xrightarrow{k_1'} C' \qquad (8)$$

where C'is inactive for the polymerization. When the reaction (8) competes with the initiation step, the catalyst concentration effective for the polymerization should be expressed as in the equation (9).

$$C = \frac{k_1}{k_1 + k_1'M_o} \cdot C_o \qquad (9)$$

In this case, the final yield is expressed:

$$Y = 1 - \frac{M_\infty}{M_o}$$

$$= 1 - \exp\left\{\left(-\frac{k_2}{k_5}\right)\left(\frac{k_1}{k_1 + k_1'M_o}\right)\cdot C_o\right\} \qquad (10)$$

Equation (10) is transformed into the following:

$$\frac{1}{\ln(1 - Y)} = -\frac{k_5}{k_2}\cdot\frac{1}{C_o} - \frac{k_5}{k_2}\cdot\frac{k_1'}{k_1}\cdot\frac{M_o}{C_o} \qquad (10')$$

The results depicted in Figure 10 are replotted according to the equation (10') in Figure 12. Linearity is established between $1/\ln(1 - Y)$ and M_o and the rate constant ratios were obtained from the slope $(-k_5/k_2)$ and the intercept $(-k_5 \cdot k_1'/k_2 \cdot k_1)$.

$$\frac{k_5}{k_2} = 1.35 \times 10^{-3} \quad \text{mole/l}$$

$$\frac{k_1'}{k_1} = 1.47 \quad \text{l/mole}$$

These values suggest that the termination rate constant (k_5) is much smaller than that of the propagation (k_2), and the reaction (8) occurs as fast as the initiation reaction when the monomer concentration is around 1 mole/l, that is actually the case.

The presence of the reaction (8) is supported not only kinetically but also spectroscopically as described below. The ultraviolet spectra of the methanol soluble products recovered from the polymerization system (a) and the biscyclopentadienyl titanium dichloride (b) which was synthesized as reported,[7] are shown in Figure 13 together with that of CPD (c). Both spectra

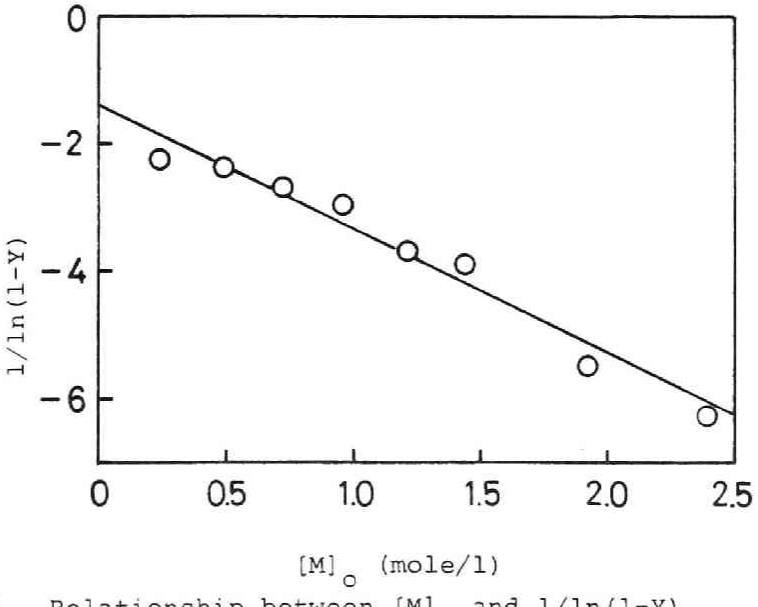


Fig. 12. Relationship between $[M]_o$ and $1/\ln(1-Y)$. From Fig. 10 and equation (10').

(a) and (b) have the maximum absorbance at 250 mμ, while CPD at 240 mμ, which suggests the formation of biscyclopentadienyl titanium dichloride in the polymerization system. When $BF_3 \cdot OEt_2$ was employed as a polymerization catalyst, no such methanol soluble products were detected in the polymerization system.

The moelcular weight of the polymer is expressed as in equation (11), taking the reaction (8) into account.

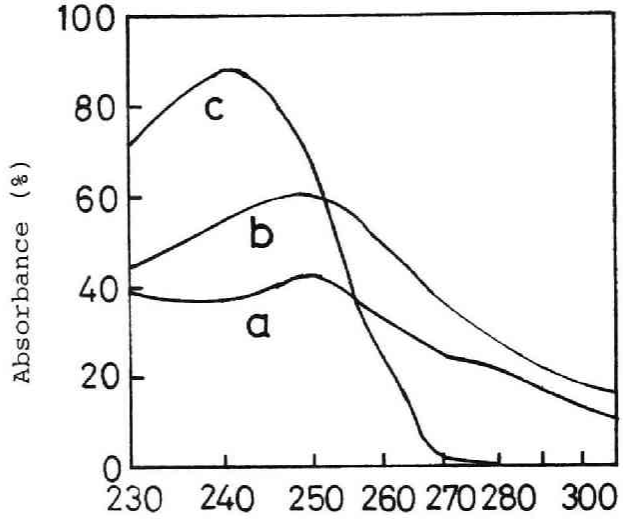


Fig. 13. UV absorption spectra in methanol solution.

a. Methanol soluble products in the polymerization system (Polymerization conditions are the same as in Fig. 8)
b. Biscyclopentadienyl titanium dichloride (ca. 0.09 mmole/l)
c. Cyclopentadiene (ca. 0.07 mmole/l)

$$\frac{1}{P_n} = \frac{k_4}{k_2} + \frac{k_3 + k_5}{k_5} \cdot \frac{k_1}{k_1 + k_1'M_o} \cdot \frac{C_o}{M_o - M_\infty} \qquad (11)$$

This equation predicts an increase of molecular weight with the decrease of the catalyst concentration, which is the observed behaviour. In most cationic polymerizations in which the stationary concentration of active species is established, the molecular weight of the polymer does not depend on the catalyst concentration. Thus the dependence of the molecular weight on the catalyst concentration is a feature of the non-stationary state polymerization in which the rate of initiation is very large.

The above discussion is based on the assumption that the effect of the water concentration in the system is possible to be ignored, but this is not the case as demonstrated in Figure 5. Water decreases the yield either in the initiation step or in the termination step, i.e.

$$TiCl_4 + H_2O \longrightarrow C'' \text{ (inactive)} \qquad k_1'' \qquad (12)$$

$$P^* + H_2O \longrightarrow P' \qquad k_5' \qquad (13)$$

Taking both equations (12) and (13) into account, the following equation could be derived:

$$\frac{1}{\ln(1 - Y)} = -\frac{k_5 + k_5'[H_2O]}{k_2} \cdot \left\{ 1 + \frac{k_1'}{k_1} \cdot M_o + \frac{k_1''}{k_1} \cdot \frac{[H_2O]}{M_o} \right\} \cdot \frac{1}{C_o} \qquad (14)$$

Figure 12 shows the linear relationship between $1/\ln(1 - Y)$ and M_o, hence the last term in the equation (14) is negligible under the present polymerization conditions. Therefore water should participate on the reaction at termination step, i.e. equation (13) is more predominant than equation (12). This means water acts as a terminator rather than as a desactivator of $TiCl_4$, which seems reasonable since in the present work TCA was always used as a cocatalyst.

Section 1.2

Polymerization with Stannic Chloride-Trichloroacetic Acid and Boron Trifluoride Etherate

INTRODUCTION

The polymerization of CPD by titanium tetrachloride-trichloroacetic acid (TCA) has been described in the previous section.[8] It was found that the polymerization rate was very large and the asymptotic yield was soon attained before all the monomers were consumed. In addition, the higher the initial monomer concentration, the lower the final yield, as a result of the formation of titanocene from CPD and $TiCl_4$ in the polymerization system.

In order to elucidate the kinetic features of the polymerization of CPD, the author extended his work to the polymerizations of CPD by $SnCl_4$-TCA and by $BF_3 \cdot OEt_2$, which are known not to produce the ferrocene type compound with CPD. This section will describe the interesting but complicated kinetic features observed in these polymerization systems and the importance of the catalyst to determine the stationary state character of the polymerization system.

EXPERIMENTAL

Reagent

Catalysts $SnCl_4$ was distilled from phosphorous pentoxide into glass ampoules. Commercial TCA (guaranteed reagent) was used without further purification. The equimolar mixture of $SnCl_4$ and TCA was used to start the polymerization. $BF_3 \cdot OEt_2$ was distilled into glass ampoules and used.

The purification of CPD and toluene were described in the previous section.[8)]

Procedures

Polymerization procedures were the same as stated in the previous section.[8)]

Polymer molecular weights were compared in terms of the intrinsic viscosity at 30°C of polymer solution either in toluene or in benzene.

RESULTS

1. Rate of Polymerization with Stannic Chloride-Trichloroacetic Acid.

Figure 1 shows the effect of the initial concentration of catalyst $[C]_o$ on the time-conversion curves of CPD polymerization with $SnCl_4$-TCA. From the initial slopes of the time-conversion curves the initial rate of polymerization (R_{p_o}) was found to be proportional to $[C]_o$.

Time-conversion curves in Figure 1 were replotted in Figure 2 in the form of log $[M]_o/[M]_t$ against t (the first-order plot),

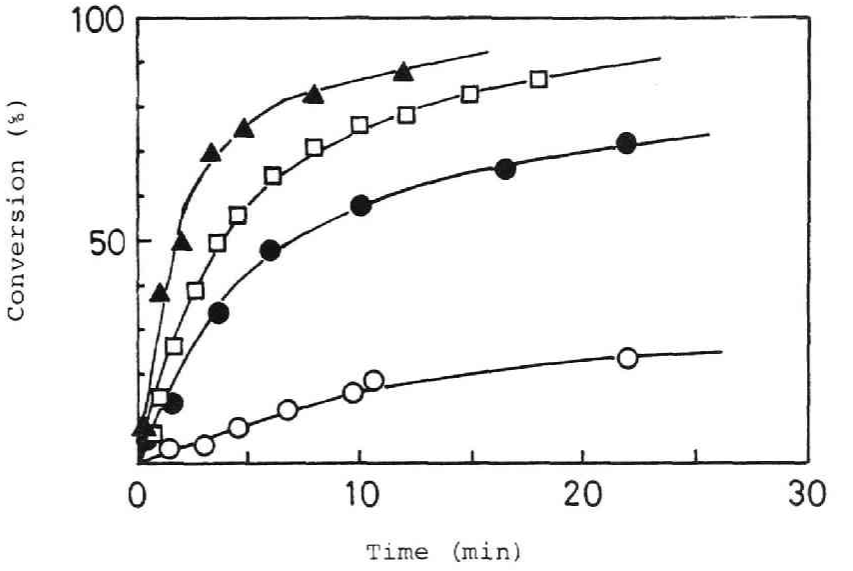


Fig. 1. Effect of $[C]_o$ on time-conversion curves for the polymerization of CPD with $SnCl_4$-TCA at -78°C. $[M]_o$ 1.5 mole/l. $[C]_o$ ▲ 5.0 mmole/l, □ 2.5 mmole/l, ● 2.0 mmole/l, ○ 1.0 mmole/l. $[H_2O]_o$ ca. 3 mmole/l. Solvent toluene.

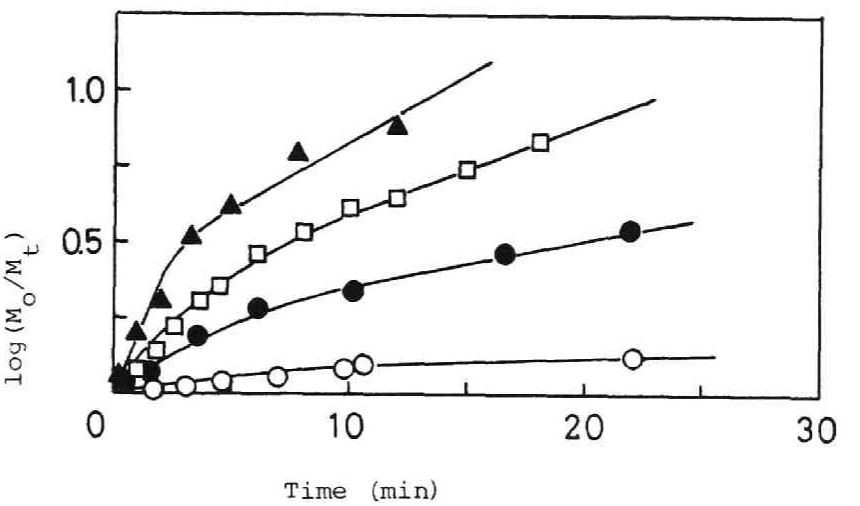


Fig. 2. Polymerization of CPD with $SnCl_4$-TCA at -78°C. The first-order plot of Fig. 1.

where $[M]_o$ and $[M]_t$ stand for the initial monomer concentration and the monomer concentration at time t, respectively. No simple linear relationship was observed between log $[M]_o/[M]_t$ and t, which means that the stationary concentration of the growing species has not been established. Similarly, the zeroth- or second-order plot of Figure 1 showed no linearity. The temperature rise during the polymerization was about 4°C. Therefore, the first rapid polymerization can hardly be accounted for by the large instantaneous temperature rise as a result of exothermic propagation reaction. $TiCl_4$-TCA as an initiator, which gave much faster initial polymerization, did not show such behavior as $SnCl_4$-TCA did.

However, it should be noted that the first-order plot in Figure 2 can be divided into two steps, i.e., the first curved section (step I) and the straight section (step II). In step I the polymerization of CPD is started with a rapid initiation reaction and the propagation reaction follows with diminishing numbers of the growing species as a consequence of termination reaction (non-stationary state polymerization). On the other hand, in step II the non-stationary state polymerization has ceased and only the stationary state polymerization is observed. In the present section quantities concerning step I and step II and the initial quantity are denoted by suffixes I, II and o, respectively. To know the effect of $[C]_o$ on the concentration of growing species at each polymerization step, the initial slopes of the step I, $\left\{(\ln[M]_o/[M]_t)/t\right\}_{I_o}$, and the slopes of the step II,

$\{(\ln[M]_o/[M]_t)/t\}_{II}$, were plotted against $[C]_o$, in Figure 3. It was found that either the initial concentration of growing species at step I or the concentration of growing species at step II was proportional to $[C]_o$.

Next, the effect of $[M]_o$ on the polymerization rate was investigated, and it was found that R_{p_o} was proportional to $[M]_o^{1.4}$. The first-order plot of the polymerization with varying monomer concentrations, which is not shown here, demonstrated the presence of two steps (step I and step II), in analogy with Figure 2.

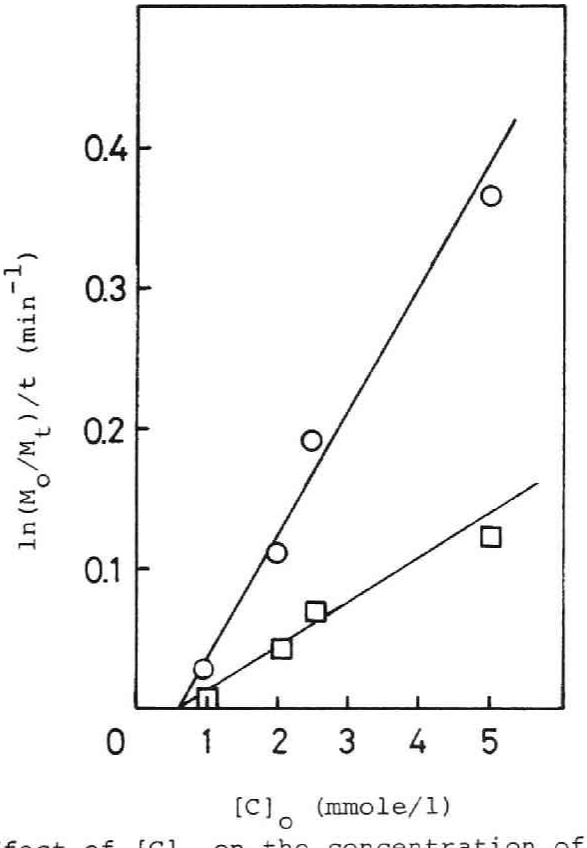


Fig. 3. Effect of $[C]_o$ on the concentration of active species at step I and step II. Polymerization conditions the same as in Fig. 1. ○ Initial slope of the first-order plot at step I. □ Slope of the first-order plot at step II.

Similarly to Figure 3, the slope of the first-order plot at each step was plotted against $[M]_o$ in Figure 4. It can be said that the initial concentration of growing species at step I is proportional to $[M]_o$, while the concentration of the growing species at step II is independent of $[M]_o$.

From the experimental evidence mentioned above it has been made clear that the cationic polymerization of CPD with $SnCl_4$-TCA occurs with either stationary or non-stationary state polymerization at the beginning, but that only the stationary state polymerization survived toward the end. In non-stationary state polymerization, $R_{p,I_o} = K_I[C]_o[M]_o^2$, and in stationary state polymerization, $R_{p,II} = K_{II}[C]_o[M]_t$.

The effect of water on the polymerization rate was investigated. The time-conversion curves and their first-order plots

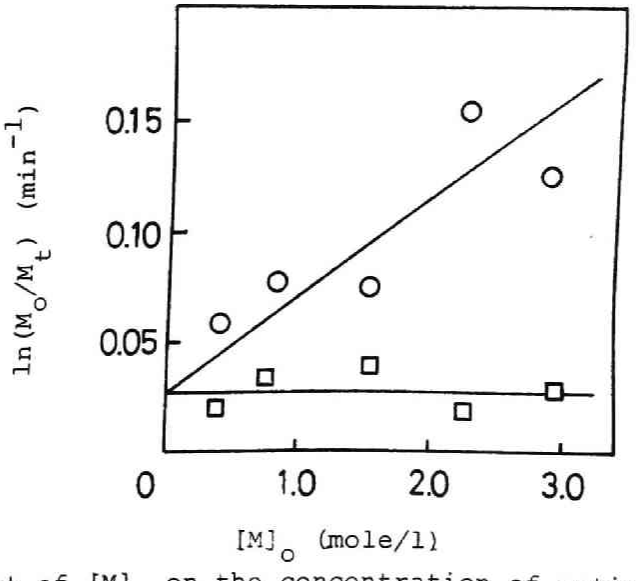


Fig. 4. Effect of $[M]_o$ on the concentration of active species at step I and step II. $[C]_o$ 2 mmole/l, $[H_2O]_o$ 4-6mmole/l, Solvent toluene. ○ Initial slope of the first-order plot at step I. □ Slope of the first-order plot at step II.

for the polymerization with varying water concentrations showed that the increase of water concentration lowered the polymerization rate a little, but that when water concentrations much exceeded the catalyst concentration the polymerization rate dropped sharply. The steps I and II under the various water concentrations were again observed.

2. Intrinsic Viscosity of Polycyclopentadiene Obtained with Stannic Chloride-Trichloroacetic Acid.

Intrinsic viscosities of polycyclopentadiene (PCPD) produced with $SnCl_4$-TCA were affected by $[C]_o$, as shown in Figure 5. The lower was $[C]_o$, the higher was the intrinsic viscosity of polymer. The effect of $[C]_o$ may be no doubt related to the non-stationary state character of the polymerization system (step I). Intrinsic

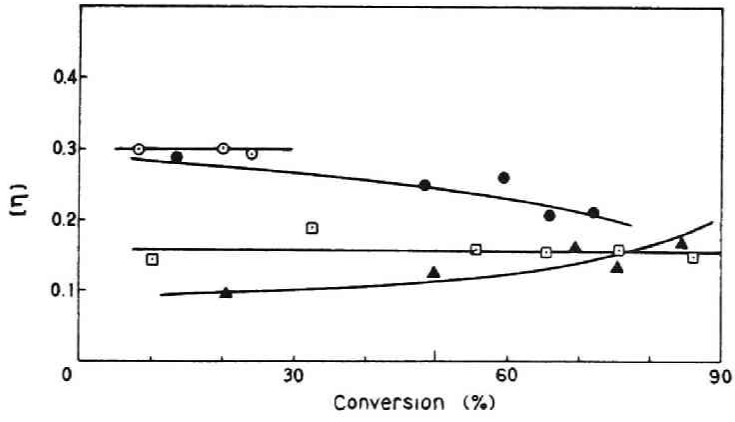


Fig. 5. Effect of $[C]_o$ on polymer intrinsic viscosity obtained with $SnCl_4$-TCA. Symbols the same as in Fig. 1.

viscosities of PCPD increased with increasing $[M]_o$.

While water affected the rate of polymerization, the viscosity of polymer was little affected by the water concentration. This fact may also be related to the non-stationary character of the polymerization system. With reference to the effects of $[C]_o$, $[M]_o$, and $[H_2O]_o$ on R_p and the intrinsic viscosity, a very similar situation, has been met in the polymerization of CPD with $TiCl_4$-TCA,[8] which was found to be non-stationary state polymerization.

3. Rate of Polymerization with Boron Trifluoride Etherate.

The polymerization of CPD catalyzed by $BF_3 \cdot OEt_2$ generally proceeded more slowly than that by $SnCl_4$-TCA. The effect of catalyst concentration on time-conversion curves is shown in Figure 6. Having determined the initial slope of each time-conversion curve, it was found that R_{p_o} was proportional to nearly 4th power of $[C]_o$.

Next, the polymerization of CPD was carried out with varying concentrations of monomer, and the time-conversion curves are determined for each monomer concentration in Figure 7. The determination of the initial slope of each time-conversion curve showed the relationship that R_{p_o} is proportional to $[M]_o^2$. As a consequence, for the polymerization with $BF_3 \cdot OEt_2$, the kinetic relationship $R_{p_o} = k[M]_o^2[C]_o^4$ was established.

The first-order plots of the time-conversion curves in Figure 7 became smooth convex curves instead of straight lines. Similar first-order plots were derived from Figure 6. These

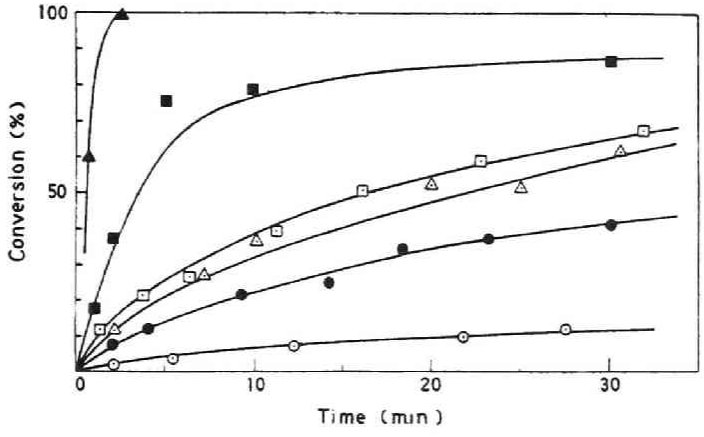


Fig.6. Effect of $[C]_o$ on time-conversion curves for the polymerization of CPD with $BF_3 \cdot OEt_2$ at -78°C. $[M]_o$ 1.5 mole/l. $[C]_o$ ▲ 30mmole/l, ■ 13 mmole/l, □ 10 mmole/l, △ 8.0 mmole/l, ● 7.5 mmole/l, ○ 5.0 mmole/l. $[H_2O]_o$ ca. 5 mmole/l. Solvent; toluene.

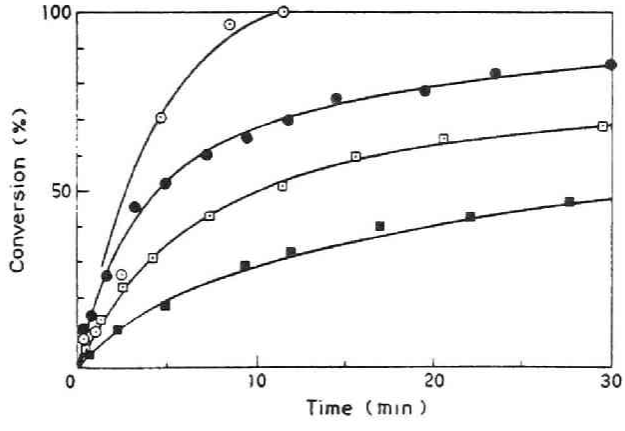


Fig. 7. Effect of $[M]_o$ on time-conversion curves for the polymerization of CPD with $BF_3 \cdot OEt_2$ at -78°C. $[C]_o$ 10 mmole/l. $[M]_o$ ○ 1.5 mole/l, ● 1.0 mole/l, □ 0.59 mole/l, ■ 0.29 mole/l.

experimental facts imply that the polymerization of CPD with $BF_3 \cdot OEt_2$ is a non-stationary one, but that the non-stationary character is much less marked than that in $SnCl_4$-TCA catalyzed polymerization because the curvature of the first-order plot was not so marked. In fact, it can be regarded as a stationary state polymerization except for the very early stage of the polymerization (see below).

With increasing amount of water the rate of polymerization catalyzed by $BF_3 \cdot OEt_2$ decreased.

4. Intrinsic Viscosity of Polycyclopentadiene Obtained by Boron Trifluoride Etherate.

In general the intrinsic viscosity of PCPD produced by $BF_3 \cdot OEt_2$ was higher than that by $SnCl_4$-TCA. The most striking feature of the PCPD obtained with $BF_3 \cdot OEt_2$ was that it was soluble in toluene but only partly soluble in benzene at room temperature, while PCPD's obtained with $TiCl_4$-TCA or $SnCl_4$-TCA were soluble in both benzene and toluene under comparable conditions. On the basis of these experimental results, toluene was used as the solvent for the viscosity measurement. The effect of monomer concentration on the intrinsic viscosity of PCPD was investigated, while the concentrations of catalyst and water were kept constant. Consequently it was found that the molecular weight of PCPD increased with increasing monomer concentration. The influence of the catalyst concentration on the intrinsic viscosity of PCPD was investigated, while the concentrations of monomer and water were kept constant. The results shown in Figure 8 indicated that the catalyst concentration affected little the intrinsic viscosity of polymer. This

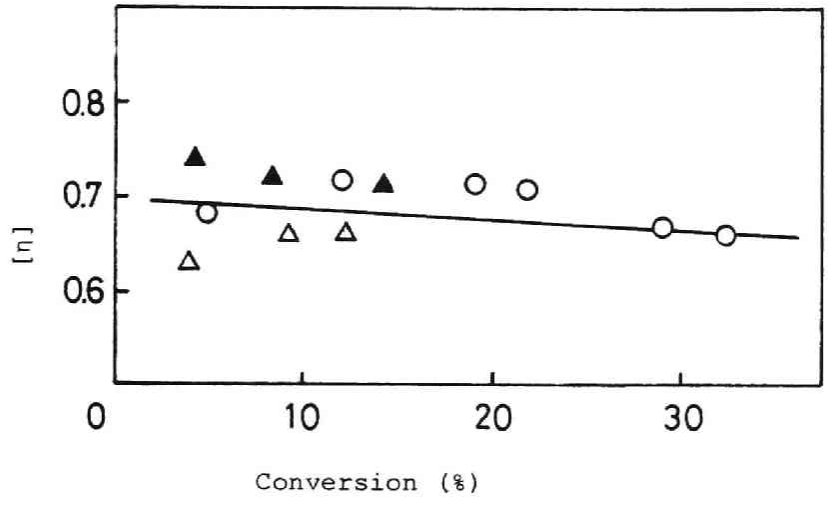


Fig. 8. Effect of $[C]_o$ on polymer intrinsic viscosity obtained with $BF_3 \cdot OEt_2$ at -78°C. $[M]_o$ 1.0 mole/l. $[C]_o$ ▲ 10 mmole/l, △ 5.0 mmole/l, ○ 3.0 mmole/l. $[H_2O]_o$ ca. 2.5 mmole/l.

has been commonly observed in a stationary state polymerization of vinyl monomers. For the last, the effect of water concentration on the intrinsic viscosity of PCPD was investigated, the concentrations of monomer and catalyst being kept constant. It was found that the intrinsic viscosity of PCPD was decreased with the increment of water concentration, in particular at low conversions, which is in marked contrast to the effect of water in $SnCl_4$-TCA catalyzed polymerization and admittedly interpreted in terms of conventional stationary state kinetics.

DISCUSSION

The polymerization of CPD with $SnCl_4$-TCA in toluene at -78°C was found to include both non-stationary and stationary state

polymerizations concomitantly. The fast initiation reaction induced by a part of catalyst molecules added led to a non-stationary state, where the initial rate of polymerization R_{p,I_o} was expressed by the following equation: $R_{p,I_o} = K_I[C]_o[M]_o^2$. On the other hand, the slow initiation reaction induced by the rest of catalyst molecules brought about stationary state polymerization, where the rate of polymerization $R_{p,II}$ was expressed by the following equation : $R_{p,II} = K_{II}[C]_o[M]_t$. In the early stage of the polymerization (step I) both mechanisms are operative, so the initial overall polymerization rate R_{p_o} appeared to be proportional to $[M]_o^{1.4}$. As the major amount of monomers is consumed in the non-stationary polymerization during step I, the molecular weight of polymer obtained with $SnCl_4$-TCA was successfully explained on the basis of the non-stationary state kinetics as indicated in section 1.1.

The nature of catalyst is very important to determine the initiation mechanism. In Table 1 the experimental results described in this chapter on the cationic polymerization of CPD are summarized, particularly in connection with the initiation mechanism. Non-stationary character in cyclic diene polymerization is more enhanced in the order $TiCl_4$-CCl_3COOH > $SnCl_4$-CCl_3COOH > $BF_3 \cdot OEt_2$, which is in agreement with the order of the acidity of metal halide.

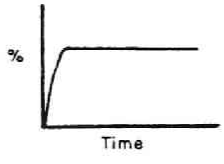
The reason why non-stationary and stationary polymerizations coexist in the polymerization catalyzed by $SnCl_4$-TCA is another point of interest. It is tentatively proposed that the order of the reaction in a termolecular reaction among a catalyst

Table I

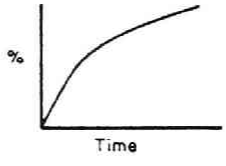
Summary of Cationic Polymerization of Cyclopentadiene

$TiCl_4$-TCA catalyst	$SnCl_4$-TCA catalyst	$BF_3 \cdot OEt_2$ catalyst
Time-conv. curve, Type A[a]	Time-conv. curve, Type B[b]	Time-conv. curve, Type C[c]
R_{P_0} : large	R_{P_0} : medial	R_{P_0} : small
$[\eta]$: 0.1-0.3	$[\eta]$: 0.2-0.5	$[\eta]$: 0.4-0.7
The higher the $[C]_0$, the lower the $[\eta]$.	The higher the $[C]_0$, the lower the $[\eta]$.	$[\eta]$ is independent of $[C]_0$.

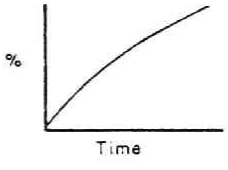
[a] Type A



[b] Type B



[c] Type C



(BF_3, $SnCl_4$ or $TiCl_4$), a cocatalyst (Et_2O or TCA), and a monomer (CPD) is important,[9] i.e.,

$$BF_3 + CPD \underset{}{\overset{K_1}{\rightleftharpoons}} BF_3 \cdot CPD \qquad (15)$$

$$BF_3 + Et_2O \overset{K_2}{\rightleftharpoons} BF_3 \cdot OEt_2 \xrightarrow[\text{slow}]{CPD} P_1^* \quad \text{nearly stationary state polymn.} \qquad (16$$

$$SnCl_4 + CPD \overset{K_3}{\rightleftharpoons} SnCl_4 \cdot CPD \xrightarrow[\text{fast}]{TCA} P_1^* \qquad \text{non-stationary state polymn.} \quad (17)$$

$$SnCl_4 + TCA \overset{K_4}{\rightleftharpoons} SnCl_4 \cdot TCA \xrightarrow[\text{slow}]{CPD} P_1^* \qquad \text{stationary state polymn.} \quad (18)$$

$$TiCl_4 + CPD \overset{K_5}{\rightleftharpoons} TiCl_4 \cdot CPD \xrightarrow[\text{fast}]{TCA} P_1^* \qquad \text{non-stationary state polymn.} \quad (19)$$

$$TiCl_4 \cdot CPD \xrightarrow{CPD} TiCl_2(C_5H_5)_2 \qquad \text{inactive catalyst} \quad (20)$$

$$TiCl_4 + TCA \overset{K_6}{\rightleftharpoons} TiCl_4 \cdot TCA \qquad (21)$$

In the postulated mechanism above, it is important that CPD is very susceptible to the complex formation with metal halide, and that $TiCl_4$ is most electrophilic, BF_3 is least electrophilic, and $SnCl_4$ is intermediately electrophilic. The above mechanism could roughly explain the experimental results mentioned in this chapter and listed in Table 1. With BF_3, $K_2 > K_1$, so that the initiation reaction proceeds almost entirely by the reaction of monomer with $BF_3 \cdot OEt_2$ complex. As the ionization of monomer by $BF_3 \cdot OEt_2$ complex is slow, the polymerization system assumes a stationary state character. With $TiCl_4$, $K_5 > K_6$ so that the initiation reaction proceeds virtually by the reaction of TCA with $TiCl_4$-CPD complex. As the protonation of $TiCl_4$-CPD complex by TCA is fast, the non-stationary state character emerges. Furthermore, $TiCl_4$ is so electrophilic that $TiCl_4$-CPD complex can react with another molecule of CPD to give biscyclopentadienyl titanium dichloride. This reaction competes with the

initiation reaction, thus leading to the leveling-off phenomenon of the time-conversion curve and the inverse proportionality of the final conversion to the initial monomer concentration.[3] With $SnCl_4$, K_3 competes with K_4, so two initiation mechanisms are operative. The protonation of $SnCl_4$-CPD complex by TCA is fast; hence the non-stationary state polymerization and $R_{p,I_o} = k_I[M]_o^2[C]_o$. On the other hand, if the protonation of monomer by $SnCl_4$-TCA complex is slow, stationary state polymerization, $R_{p,II} = k_{II}[C]_o[M]_t$, will result.

To confirm the proposed mechanism the effect of the addition of monomer and catalyst on the time conversion curve was investigated. The polymerization of CPD was started with $SnCl_4$-TCA. When the polymerization came to about 80 % conversion and only a stationary state polymerization was operative, CPD was added. The change of the time-conversion curve is shown in Figure 9 as a first-order plot. Non-stationary state polymerization was observed, as expected, as a consequence of the shift of the equilibrium (17) to the right. On the other hand, as is seen in Figure 9, the addition of a small amount of $SnCl_4$-TCA did not bring about non-stationary state polymerization but stationary state polymerization with increased concentrations of the active species. This is exactly what we expected, because the formation of $SnCl_4$-CPD complex is unfavored when both the catalyst and the monomer concentrations are low. The effect of catalyst addition on polymerization was further studied in some details. When the polymerization of CPD catalyzed by $SnCl_4$-TCA reached about 75 %

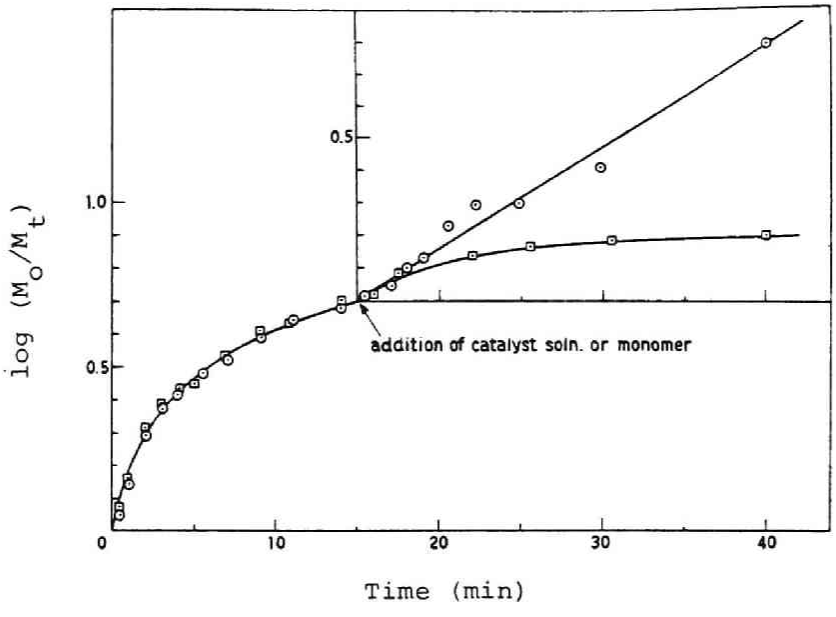


Fig. 9. Effect of the addition of catalyst or monomer on the polymerizing system of CPD with $SnCl_4$-TCA. $[M]_o$ 1.5 mole/l, $[C]_o$ 2.0 mmole/l. O Experiment of catalyst addition; added catalyst, 2.0 mmole/l. □ Experiment of monomer addition; [M] after monomer addition, 1.6 mole/l.

conversion, a fairly large amount of catalyst ($SnCl_4$ and TCA) was added. Although the concentration of residual monomer was low, a high catalyst concentration made the formation of $SnCl_4$-CPD complex [Eq. (17)] rather important. Accordingly, the reproduction of the non-stationary state was observed a little. When the catalyst ($SnCl_4$ and TCA) was added at low conversions, the non-stationary state character of the subsequent polymerization was very marked. This is what we expected from Eq. (14), because in this case both monomer and catalyst concentrations were high. These experimental results support the initiation mechanism postulated above. The coexistence of non-stationary and stationary

polymerizations has been suggested also by Blake and Eley[10] with regard to the alkyl vinyl ether-$BF_3.OEt_2$ system, in which very nucleophilic monomer is also involved.

Although the kinetic data can be interpreted in the present manner, it should be pointed out that the conclusions need to be supported by other data to be firm.

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Chapter 2

Methylcyclopentadiene

INTRODUCTION

It is interesting to note that cyclic dienes, in particular cyclopentadiene (CPD), are highly reactive in cationic polymerization though they have no strongly electron-donating group like other reactive monomers in cationic polymerization.[1,2] Moreover, CPD undergoes a propagation reaction in more than one way, that is 1,2- and 1,4-propagations. The problem concerning the mode of propagation can be solved in principle by analyzing the polymer structure, but with CPD it has not been settled definitely.[3]

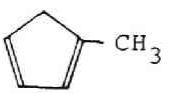
Here, in an attempt to study about the reactivity of alkyl substituted cyclic dienes, the polymerization of methylcyclopentadiene (MCPD) was investigated. As far as we are aware, only a preliminary investigation on the polymerization of MCPD has been reported.[4] In the present investigation the author, directed his attention primarily to the effect of the methyl substituent on the reactivity of monomer and on the structure of the polymer obtained. Some discussion of the mechanism of the initiation reaction is also given.

EXPERIMENTAL

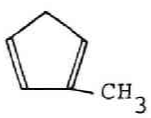
Materials

MCPD was obtained by the pyrolysis of the dimer, which was purified by vacuum distillation. The MCPD was collected and stored at -78°C and was distilled from calcium hydride just before use (b.p. 70–71°C). As will be shown later, the MCPD thus obtained was a mixture of two isomers. The composition of MCPD was analyzed by gas chromatography according to Csicsery[5] on a dimethyl sulfolane column at 36°C.

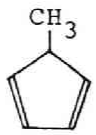
Three isomers are known for MCPD[5]: the 1-methyl-, 2-methyl-, and 5-methylcyclopentadienes.



1-Methylcyclopentadiene



2-Methylcyclopentadiene



5-Methylcyclopentadiene

The gas chromatogram of MCPD obtained by pyrolysis of the dimer revealed that the MCPD used for the present investigation was a mixture consisting of 52 % 2-MCPD, 45 % 1-MCPD, and 3 % CPD. The content of CPD varied slightly, depending on the conditions of pyrolysis, but the ratio of 1-MCPD and 2-MCPD kept always unchanged.

The isomerization of monomer during the polymerization may not be important, because the polymerization rate is quite large, as is seen in Figures 1–3, whereas the isomerization rate at low

temperatures has been reported to be slow.[6)]

The purification of CPD has been described.[1)]

Titanium tetrachloride ($TiCl_4$) stannic chloride ($SnCl_4$), and boron trifluoride etherate ($BF_3 \cdot OEt_2$) were used as catalysts and were distilled directly into glass ampules (in the case of $SnCl_4$, from phosphorus pentoxide). Commercial trichloroacetic acid (TCA) was used as a cocatalyst without further purification. The mole ratio of the acid to metal halides was always unity.

Toluene and sometimes methylene chloride were used as solvents They were purified as usual. The water content of the solvent was 3–5 mmole/l as determined by the Karl Fischer method.

Procedures

The polymerizations were carried out at -78°C. The polymerization apparatus and the procedures have been described in Chapter 1. The intrinsic viscosity of benzene solution of polymethylcyclopentadiene (PMCPD) was measured at 30°C. Infrared spectra of the polymer were measured on the carbon disulfide solutions or KBr disks. Nuclear magnetic resonance (NMR) spectra of the polymer were measured as carbon tetrachloride solutions at 60 MHz against tetramethylsilane as an internal standard.

RESULTS

1. Homopolymerization of Methylcyclopentadiene.

Time-conversion curves for the polymerization of MCPD with $TiCl_4$-TCA are shown in Figure 1. The polymerization was very rapid at first, but soon it stopped at a certain conversion which

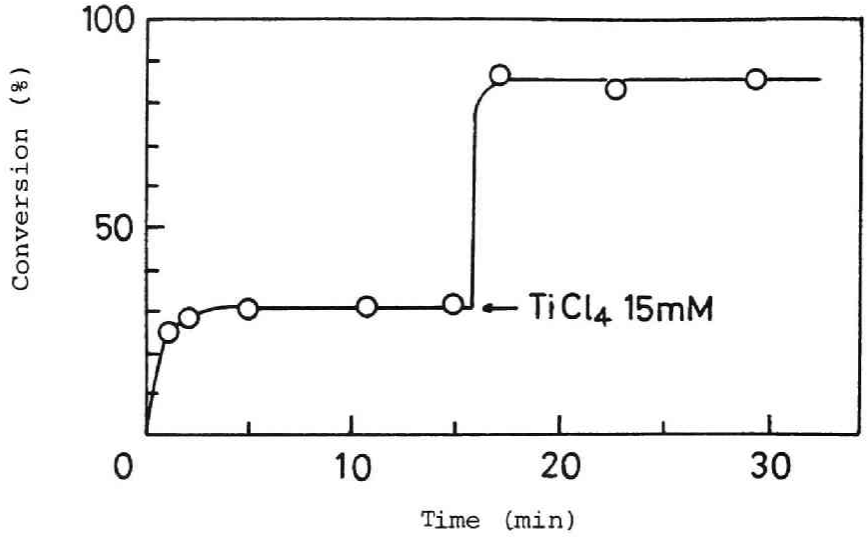


Fig. 1. Polymerization of MCPD with $TiCl_4$-TCA at -78°C. $[M]_o$ 1.2 mole/l, $[C]_o$ 6.0 mmole/l, Solvent toluene. Additional $TiCl_4$ added as indicated in the figure.

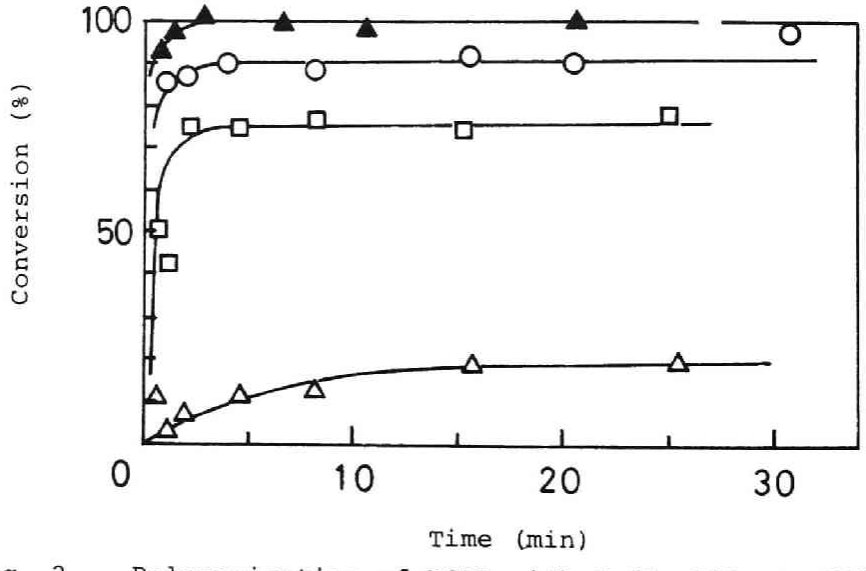


Fig. 2. Polymerization of MCPD with $SnCl_4$-TCA at -78°C. $[C]_o$; △ 0.53 mmole/l, □ 1.1mmole/l, ○ 2.4 mmole/l, ▲ 6.0 mmole/l. $[M]_o$ 1.2 mole/l. Solvent toluene.

depended on the initial catalyst concentration. It is therefore evident that the polymerization is of typical non-stationary state type started with a fast initiation reaction accompanied with some termination reaction. Further addition of $TiCl_4$ to the dormant system reinitiated the rapid polymerization, which stopped again at a higher conversion. The same phenomenon was observed in the polymerization of CPD with the same catalyst.[1)]

As is seen in Figure 1, 6 mmole/l of $TiCl_4$ was needed to reach 30 % conversion of MCPD, while in the case of CPD only 1 mmole/l was needed to get the same conversion under comparable conditions.[1)] These findings may be explained by either a lower reactivity of MCPD than CPD or the more violent catalyst consumption with MCPD than with CPD.

The time-conversion curves for the polymerization of MCPD with $SnCl_4$-TCA are shown in Figure 2. Here again, a rapid initial polymerization and a saturation phenomenon of the conversion curve were observed. Hence, the polymerization of MCPD catalyzed by $SnCl_4$-TCA is also of a typical non-stationary state polymerization started with a fast initiation reaction accompanied with some termination reaction. This is in contrast to the polymerization of CPD catalyzed by $SnCl_4$-TCA,[2)] where the time-conversion curve did not level off but reached 100 % conversion. As compared with the CPD—$SnCl_4$-TCA system,[2)] a much smaller amount of catalyst was enough to bring the polymerization of MCPD to higher conversions under comparable conditions. Therefore, it seems that MCPD is more reactive than CPD.

In the polymerization of MCPD with $BF_3 \cdot OEt_2$, the initial

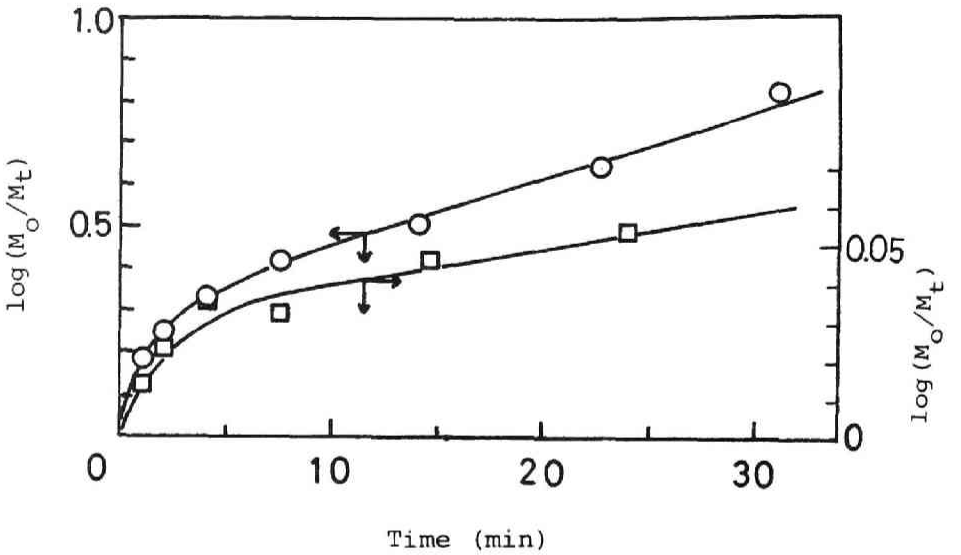


Fig. 3. Polymerization of MCPD with $BF_3 \cdot OEt_2$ at -78°C. (first-order plot). $[C]_o$ □ 2.0 mmole/l, ○ 5.0 mmole/l. $[M]_o$ 1.2 mole/l. Solvent toluene.

polymerization was rapid but the polymerization rate decreased towards the end. However, the polymerization proceeded without stopping before 100 % conversion. The plots of log ($[M]_o/[M]_t$) against t, where $[M]_o$ and $[M]_t$ represent the initial monomer concentration and the residual monomer concentration at time t, respectively, are shown in Figure 3. Here, the curves can be divided into two parts. One of them is the first curved stage which represents a non-stationary state polymerization, and the other is the latter linear stage which represents a stationary state polymerization. The same situation was met in the polymerization of CPD catalyzed by $SnCl_4$-TCA.[2] With $BF_3 \cdot OEt_2$, a larger amount of catalyst was required in CPD polymerization[2] than in MCPD polymerization to attain the same conversion under the

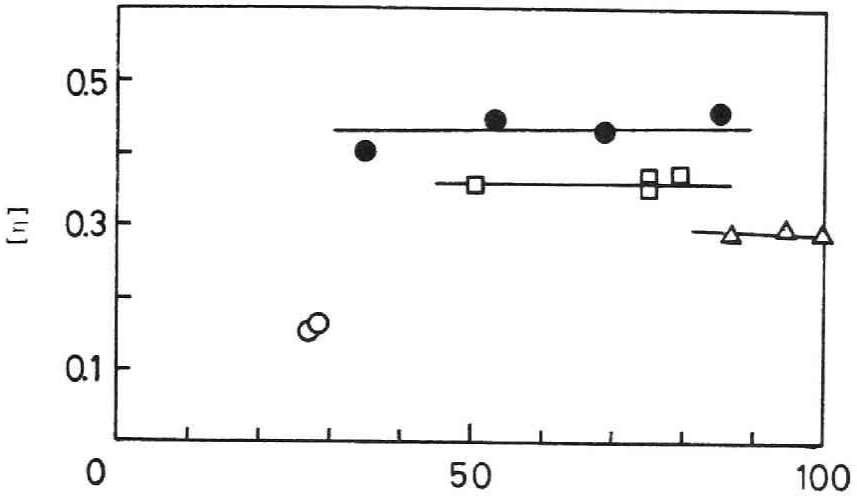


Fig. 4. Intrinsic viscosity at 30°C of benzene solution of PMCPD obtained by cationic catalysts. ○ $TiCl_4$-TCA, 6.0 mmole/l; △ $SnCl_4$-TCA, 2.4 mmole/l; □ $SnCl_4$-TCA, 6.0 mmole/l; ● $BF_3 \cdot OEt_2$, 5.0 mmole/l. $[M]_o$ 1.2 mole/l. Polymerization solvent; toluene.

comparable conditions. Therefore, MCPD appeared to be more reactive than CPD.

Figure 4 shows intrinsic viscosities of PMCPD. Since the catalyst concentration was not always constant in these polymerizations, this cannot be discussed on a quantitative level. However, it is evident that the intrinsic viscosity of the polymer is not affected by the conversion, but that it was affected by the nature of catalyst and decreased in the order $BF_3 \cdot OEt_2$ > $SnCl_4$-TCA > $TiCl_4$-TCA. This is in agreement with the order found with polycyclopentadiene (PCPD).[1,2] It can be said that the more acidic the catalyst, the lower the molecular weight of PMCPD.

2. Structure of Polymethylcyclopentadiene.

The infrared spectrum of PMCPD obtained with $TiCl_4$-TCA is shown in Figure 5. PMCPD obtained with other catalysts gave almost the same spectrum. In Figure 5 the infrared spectrum of PCPD is also shown for the comparison. Three distinct differences were observed between the two spectra. Firstly, the C–H stretching absorption at 3030 cm^{-1} was weaker in PMCPD than in PCPD. Secondly, the C=C stretching absorption of PMCPD appeared at 1680 cm^{-1}, while that of PCPD appeared at 1640 cm^{-1}. Thirdly, C–H out-of-plane deformation absorption appeared at 830 cm^{-1} with PMCPD, but at 720 cm^{-1} with PCPD. These differences are attributed to trisubstitution of the double bond in PMCPD and cis disubstitution of that in PCPD.[7] The absorption band at 1030 cm^{-1} is detectable with PMCPD. Its absorbance was proportional to the concentration of PMCPD. However, the assignment is not elear.

The NMR spectrum of PMCPD obtained with $TiCl_4$-TCA is shown in Figure 6. The spectrum is almost identical with that obtained with $SnCl_4$-TCA. The NMR spectrum of PCPD is also shown for the comparison. A sharp peak at τ 8.4 (peak D) is due to methyl protons, which is shifted downfield. A peak at τ 4.9 (peak A) is due to olefin protons, which is shifted upfield. Furthermore, the ratio of peak area A/(B + C + D) was exactly 1/7. These facts confirm that the methyl group is in conjugation with double bond, that is, the double bond is trisubstituted.[8] A small shoulder appeared at τ 4.9 (peak A). Similar splitting was sometimes observed with PCPD.[3] Since MCPD as well as CPD undergoe

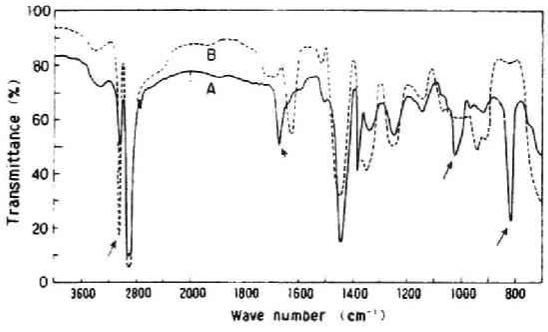


Fig. 5. Infrared spectra of PMCPD and PCPD. (A) PMCPD obtained with $TiCl_4$-TCA; (B) PCPD obtained with $TiCl_4$-TCA. Measured as KBr pellet.

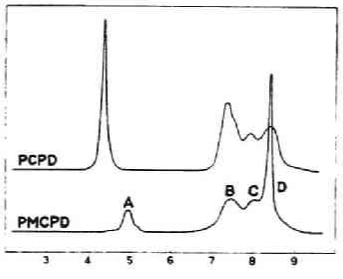


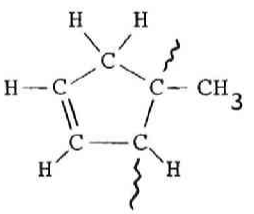
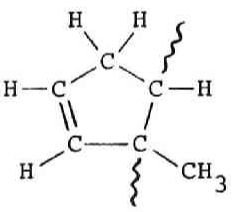
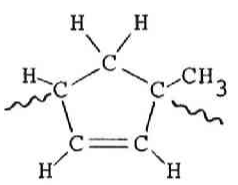
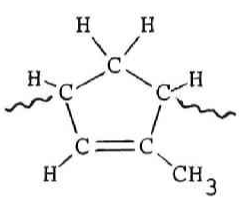
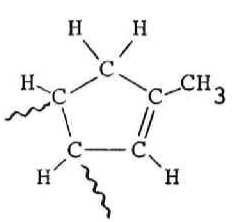
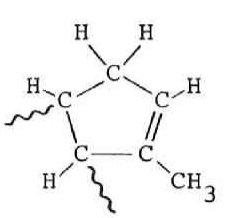
Fig. 6. NMR spectra of PMCPD and PCPD. PMCPD obtained with $TiCl_4$-TCA; PCPD obtained with $BF_3 \cdot O(C_2H_5)_2$. Measured in carbon tetrachloride solution at room temperature at 60 MHz, tetramethylsilane used as internal standard.

a propagation reaction in several ways (see below), a multiplicity of the environment of the olefinic proton may have caused the splitting of the absorption peak. Two peaks at τ 8.0 (peak C) and 7.5 (peak B) may be assigned to methylene protons and methine protons, respectively. It is possible that there is some contribution of β-methylene protons to peak D.

The MCPD used in the present investigation was the mixture of two isomers. For each isomer, 1,2-, 1,4-, and 3,4-propagation reactions, are possible, thus giving six basic structures of monomer unit in polymer, as shown in Table I. However, infrared and NMR spectra indicated that only structures IV, V, and VI are possible. If complete assignment of the peaks B and C is made and the degree of contribution of β-methylene protons to peak D is estimated, the relative abundance of structures IV, V, and VI can be quantitatively determined. However, this was not the case. Yen assigned peak B to α-protons, peak C to β-protons and peak D to methyl protons. Calculating the ratio α-H/β-H Yen concluded that the polymer has almost entirely a 1,4-structure.[4] However, the assignment of Yen for PMCPD as well as for PCPD is open to question.[3] Hence, the quantitative analysis of the polymer structure is not yet completed.

TABLE I

Structure of Polymethylcyclopentadiene

	1—MCPD			2—MCPD		
	Structure		A/(B + C + D)	Structure		A/(B + C + D)
1,2 Addition	I		1/3	II		1/3
1,4 Addition	III		1/3	IV		1/7
3,4 Addition	V		1/7	VI		1/7

DISCUSSION

The present investigation of homopolymerization of MCPD demonstrates that MCPD as well as CPD is a reactive monomer. It may generally be said that five-membered cyclic dienes are reactive in cationic polymerization. As the CPD ring does not suffer much internal strain,[9] the release of strain by conversion from a cyclic diene into a cyclic olefin at a polymerization does not explain their high reactivity. The high stability of a cyclopentenyl cation seems attractive as a reason. Thus, the pK_a value for protonated CPD (a cyclopentenyl cation, $pK_a = -8.7$) is larger than that of a protonated isobutene (a tertiary butyl cation, $pK_a = -15.5$[10]) and almost equal to that of a protonated 2,4,6-trimethyl-α-methyl-styrene ($pK_a = -7.4$[11]). These facts imply that a cyclopentenyl cation is relatively stable and cyclopentadienes are easily converted into protonated forms, which leads to a very rapid initiation reaction. The nucleophilicity of the monomer is another important factor in determining the monomer reactivity, that is, the reactivity in the propagation reaction. Introduction of methyl group augments either the stability of cyclopentenyl cation or the nucleophilicity of CPD. Consequently, MCPD interact more strongly with metal halides and is polymerized faster than CPD.

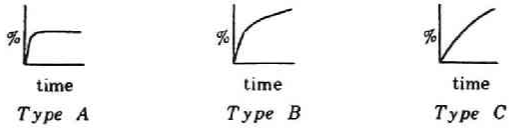
In the investigations on the homopolymerization of MCPD with various catalysts, the shape of the time-conversion curve was strongly dependent on the catalyst used as indicated for CPD in Chapter 1. These curves are classified in Table II, in which CPD is also listed for comparison. In Table II, type A is for a

TABLE II

Shape of Time-Conversion Curves

Monomer	Catalyst	Type of time-conversion curve[a]
MCPD	$TiCl_4$-TCA	A
MCPD	$SnCl_4$-TCA	A
MCPD	$BF_3 \cdot OEt_2$	B
CPD	$TiCl_4$-TCA	A
CPD	$SnCl_4$-TCA	B
CPD	$BF_3 \cdot OEt_2$	C

a



Type A *Type B* *Type C*

typical non-stationary state polymerization (fast initiation and propagation with diminishing numbers of active species), type B is for concomitant non-stationary and stationary state polymerization, and type C is for a nearly stationary state polymerization. The mechanism of the initiation reaction was investigated and is discussed in more detail in the previous chapter. It is interesting to note that the more reactive MCPD brought about a fast initiation reaction (type A) even with a less electrophilic Lewis acid ($SnCl_4$).

Study of the polymer structure indicates that the polymerization of MCPD did not proceed via a stable tertiary carbonium ion, that is, the addition of incoming monomer did not occur at a carbonium ion bearing a methyl group. This is explained in terms of steric hindrance of a methyl group if one takes into account that trisubstituted ethylenes are reluctant to be polymerized.[12] It is quite interesting that with 1-methylcyclopentadiene there is a convenient pathway for the propagation reaction which is facilitated by the electronic effect of a methyl group and without involving steric hindrance of a methyl group, because the reaction site is in conjugation with but distant from the methyl group.

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Chapter 3

1,3-Cycloheptadiene

INTRODUCTION

Polymerizations of cyclopentadiene and of methycyclopentadiene were already described.[1,2] The polymerization of 6-membered conjugated cyclic diene i.e. 1,3-cyclohexadiene has also been reported.[3] As an extension to these studies, the polymerization of 1,3-cycloheptadiene was attempted to made clear the influence of ring size on the reactivity, but there has been no report on the polymerization of this monomer. So the polymerization of 1,3-cycloheptadiene by various initiators was firstly investigated. Then the cationic polymerization of this monomer was studied and the peculiar structure of the cationically obtained polymer was suggested.

EXPERIMENTAL

Materials

Monomers 1,3-Cycloheptadiene (CHPD, b.p. 121.5–122°C) was synthesized from 1,3,5-cycloheptatriene according to the literature.[4] The purity was determined by gas chromatography to be higher than 98 %. Commercial styrene was washed and

distilled as usual.

Initiators Purifications of $SnCl_4$, $TiCl_4$ and $BF_3 \cdot OEt_2$ were already described in Chapter 1. Commercial azoisobutyronitrile was recrystalized from methyl alcohol. Commercial Et_3Al, trichloroacetic acid (TCA) and n-BuLi in hexane were used without further purification.

Solvents Toluene, methylene chloride, tetrahydrofuran and n-hexane were purified by the usual methods and used as solvents.

Procedures

Radical Polymerization Glass ampoule containing monomer and initiator was sealed off under high vacuum and placed in a bath which was maintained at 70°C.

Anionic Polymerization Solvent, initiator solution, and monomer were introduced into a glass ampoule under a dry nitrogen atmosphere and sealed off under vacuum.

Coordination Polymerization Et_3Al in n-hexane and $TiCl_4$ were introduced into a glass ampoule and aged. After the monomer solution was added, it was sealed off under vacuum and placed in a water bath at 50°C. The polymerization solution was agitated by rotating the ampoule at a speed of 24 r.p.m.

Cationic Polymerization Cationic polymerizations were carried out under a dry nitrogen atmosphere. In the case of the copolymerization of CHPD with styrene, consumption of the monomers was determined by gas chromatography (Column, dinonyl phthalate; column temperature, 95°C).

Analyses of the Polymers

NMR spectra of the polymer were measured as carbon tetrachloride solutions at 100 MHz against tetramethylsilane as an internal standard. Ultraviolet (UV) spectra of the polymer were measured as cyclohexane solution and infrared (IR) measurements were carried out on KBr pellets.

Molecular weights of the polymer were determined by vapour pressure osmometer.

RESULTS AND DISCUSSION

1. Polymerization Behaviour of 1,3-Cycloheptadiene.

In Table I is shown the polymerization of CHPD by various

Table I

Polymerization of CHPD

Initiator	Solvent	Temp. °C	Time	$[M]_o$ mole/l	$[C]_o$ mmole/l	Yield[a] %
AIBN[b]	bulk	70	20 hrs.	9.4	35	trace
"	"	"	7 days	"	"	"
n-BuLi	THF	25	20 hrs.	1.9	12	"
"	"	"	7 days	"	"	45
$AlEt_3 \cdot TiCl_4$ (2/1)	n-hex.[c]	50	3.5 hrs.	5.6	200	8
$SnCl_4$-TCA (1/1)	CH_2Cl_2	0	10 min.	0.42	20	24
"	"	"	2 hrs.	"	"	49

[a] Yield of the methanol insoluble product.
[b] azoisobutyronitrile. [c] n-Hexane.

initiators. As can be seen from Table I, the radical initiator did not produce a polymer, the anionic catalyst initiated the polymerization in a very slow rate, the Ziegler-Natta type catalyst was moderately active, and the cationic initiator was the most active to induce a fast polymerization. CHPD is much susceptible to cationic initiators as other cyclic dienes are.[1,2,3]

2. Cationic Polymerization of 1,3-Cycloheptadiene.

The cationic polymerizations of CHPD under various conditions were carried out and the results are shown in Figure 1. As

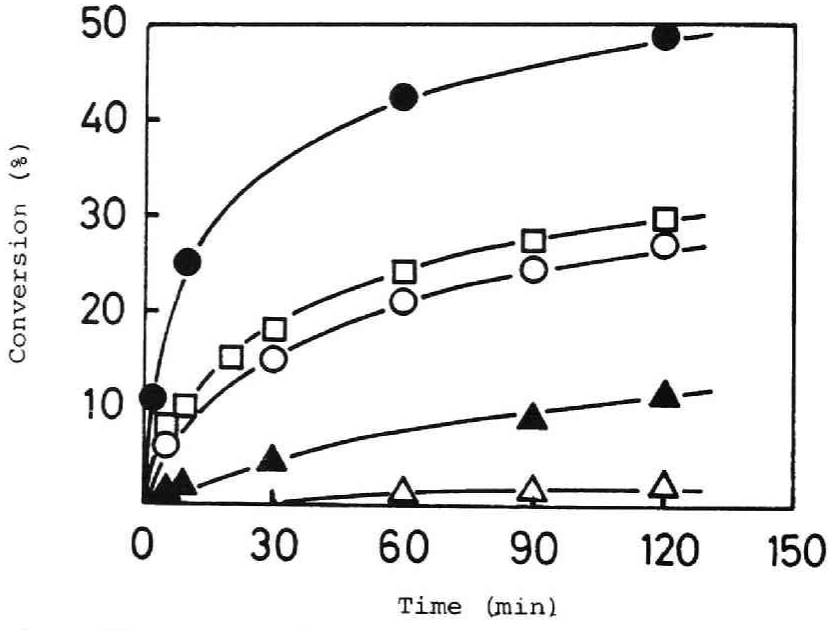

Fig. 1. Time-conversion curves for the polymerization of CHPD. $[M]_o$ 0.54 mole/l. ●; $SnCl_4$-TCA, $[C]_o$ 20 mmole/l, CH_2Cl_2, 0°C. □; $SnCl_4$-TCA, $[C]_o$ 10 mmole/l, CH_2Cl_2, 0°C. ○; $SnCl_4$-TCA, $[C]_o$ 10 mmole/l, CH_2Cl_2, -78°C. ▲; $BF_3 \cdot OEt_2$, $[C]_o$ 20mmole/l, CH_2Cl_2, 0°C. △; $BF_3 \cdot OEt_2$, $[C]_o$ 20 mmole/l, benzene, 0°C.

generally accepted in the cationic polymerization, $SnCl_4$-TCA system was more effective initiator than $BF_3 \cdot OEt_2$, and the rate was much larger in more polar solvents. The polymerization was affected little by the temperature. First-order plot of the polymerization of CHPD by $SnCl_4$-TCA or by $BF_3 \cdot OEt_2$ is shown in Figure 2. $SnCl_4$-TCA induces a non-stationary polymerization (stationary concentration of active species is not established), while $BF_3 \cdot OEt_2$ led to a stationary polymerization as judged from

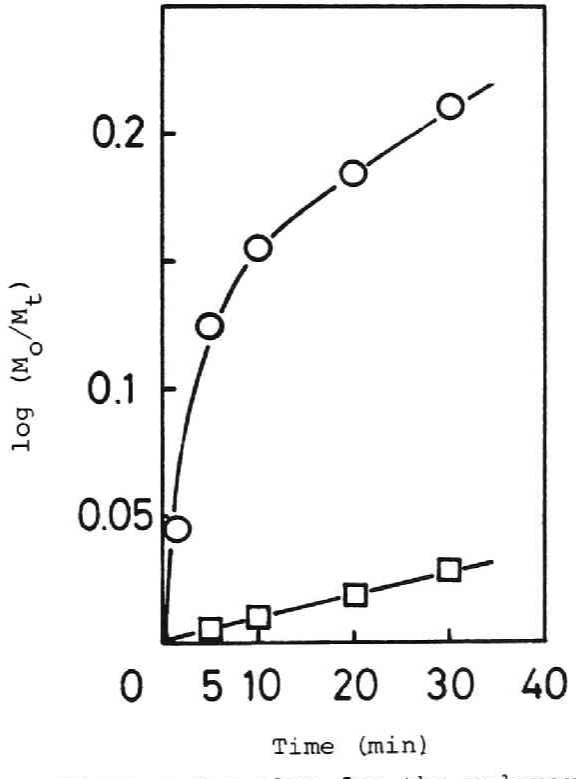

Fig.2. First-order plot for the polymerization of CHPD. $[M]_o$ 0.54 mole/l. ○; $SnCl_4$-TCA, $[C]_o$ 20 mmole/l, CH_2Cl_2, 0°C. □; $BF_3 \cdot OEt_2$, $[C]_o$ 20 mmole/l, CH_2Cl_2, 0°C.

the linearity of the first-order plot. This is in agreement with the trend described in Chapter 1, that is, $SnCl_4$-TCA is more electrophilic for cyclic dienes than $BF_3 \cdot OEt_2$ and consequently the polymerization of cyclic dienes by $SnCl_4$-TCA is non-stationary while that by $BF_3 \cdot OEt_2$ nearly stationary.

The molecular weights of the polymers obtained in the cationic polymerizations are indicated in Table II. All the

Table II

Molecular Weight of Poly-CHPD[a]

Polymerization solvent	Polymerization temperature, °C	$[M]_o$ mole/l	$[C]_o$ mmole/l	Mol. wt.
toluene	0	0.5	20	670
"	-78	"	20	1110
methylene chloride	0	0.19	"	670
"	"	0.37	"	880
"	"	0.72	"	980
"	"	0.84	5	1370
"	"	"	10	1012
"	"	"	20	1000
"	-78	"	30	1310

[a] Measured by vapour pressure osmometer.

polymers were low molecular weight ones, to which monomer transfer reactions should be responsible. In fact, from the plot of $1/M_o$ *vs.* 1/DP (Mayo plot) the rate constant ratios k_{tm}/k_p and k_t'/k_p is calculated as follows:

$$k_{tm}/k_p = 8 \times 10^{-2}$$

$$k_t'/k_p = 1.1 \times 10^{-2} \quad \text{mole/l}$$

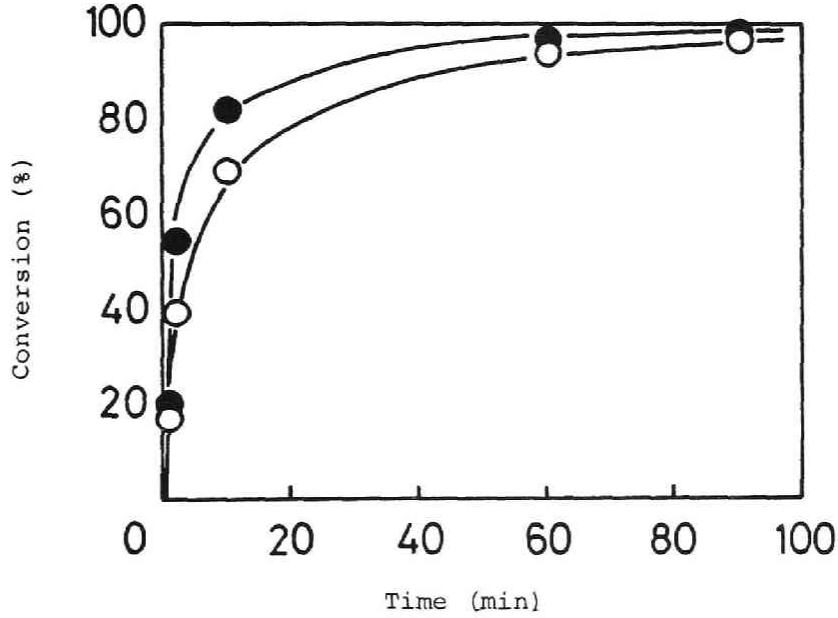

Fig. 3. Time-conversion curves for the copolymerization of CHPD (M_1) with styrene (M_2) by $SnCl_4$-TCA in CH_2Cl_2 at 0°C. $[C]_o$ 20 mmole/l, $[M_1]_o$ 0.38 mole/l, $[M_2]_o$ 0.43 mole/l. ○ styrene, ● CHPD.

The k_{tm}/k_p of styrene under the comparable conditions has been reported to be 0.53×10^{-2}.[5] Monomer transfer reaction seems to be important in the cationic polymerization of CHPD.

To estimate the relative reactivity of CHPD, the copolymerization of CHPD with styrene was carried out and the result is shown in Figure 3. CHPD was consumed a little more rapidly than styrene. According to the method of Sakurada,[6] monomer reactivity ratios are determined as follows:

$$r_{CHPD} = 1.48$$

$$r_{styrene} = 1.38$$

Thus CHPD seems to be as reactive as styrene in the cationic copolymerization. In Table III the monomer reactivity ratios

Table III

Monomer Reactivity Ratios of Cyclic Dienes

M_1	M_2	Polymerization			r_1	r_2	Ref.
		Temp., °C	Initiator	Solvent			
CPD[a]	Isobutene	-78	$SnCl_4$–TCA[a]	CH_2Cl_2	1.55	0.80	7)
CHXD[b]	"	"	"	"	1.07	0.98	"
CHXD[b]	styrene	0	$BF_3 \cdot OEt_2$	"	0.77	0.53	8)
CHPD	"	"	$SnCl_4$–TCA	"	1.48	1.38	this work

[a] Cyclopentadiene, [b] 1,3-Cyclohexadiene

relevant to the present discussion are shown. These values indicate that the reactivity of cyclic dienes falls in the following order:

CPD > CHXD > CHPD

The reactivity decreases with the increase of ring size. This relation between the structure and the reactivity will be discussed in Chapter 7.

3. Structure and Properties of the Polymers.

The NMR spectra of the polymers are shown in Figure 4. The spectrum of the polymer obtained in the cationic polymerization revealed the signal of olefinic protons much less than the theoretical. The signal at 7.92 τ is assignable to α-methine and/or α-methylene protons. The ratios of non-olefinic protons to olefinic protons are set out in Table IV. Besides the NMR data, UV absorption data and the softening points of the polymers are also indicated. IR spectra of the polymer were consistent with the NMR data, i.e., the relative intensity of the absorption at 3030 cm^{-1} due to the olefinic C—H stretching vibration was low in the cationic polymer as compared with the anionic polymer, and the absorption at 1630 cm^{-1} due to the C=C stretching vibration was somewhat smaller than expected.

Difference was also found in the UV spectra of the polymer. The anionic polymers showed only one absorption maximum at 207 nm, while the cationic polymers showed two absorption maxima at ca. 210 nm and 255 nm. The latter can perhaps be assigned to the $\pi \longrightarrow \pi^*$ transition of conjugated double bonds. These

Table IV

Polymerization Conditions and Properties of Poly-CHPD

Polymerization			NMR[a]	UV[b]	Softening point[c]
Initiator	Solvent	Temp., °C	H/H_o	nm	°C
n-BuLi	THF	25	3.94	207	95–100
$SnCl_4$-TCA[d]	toluene	50	14.3	206,253	———
"	"	0	10.9	212,254	———
"	CH_2Cl_2	"	11.3	212,256	190–195
"	toluene	-78	10.6	———	———
1,3-cycloheptadiene			1.5	244	———
cycloheptene			5.0	200,220	———

[a] Ratio of methine and methylene protons to olefinic protons....

[b] Maximum absorption in cyclohexane solution.

[c] Based on the optical observation on a micro melting point apparatus.

[d] Trichloroacetic acid.

differences in the structure reflected on the physical properties of the polymer. The large difference in the softening point of the polymers is demonstrated in Table IV.

From these results, four structures were proposed for the polymer, which are depicted in Figure 5. The polymer obtained in the anionic polymerization was proved to have two olefinic protons per one monomer unit, which corresponds to the structures I and/or

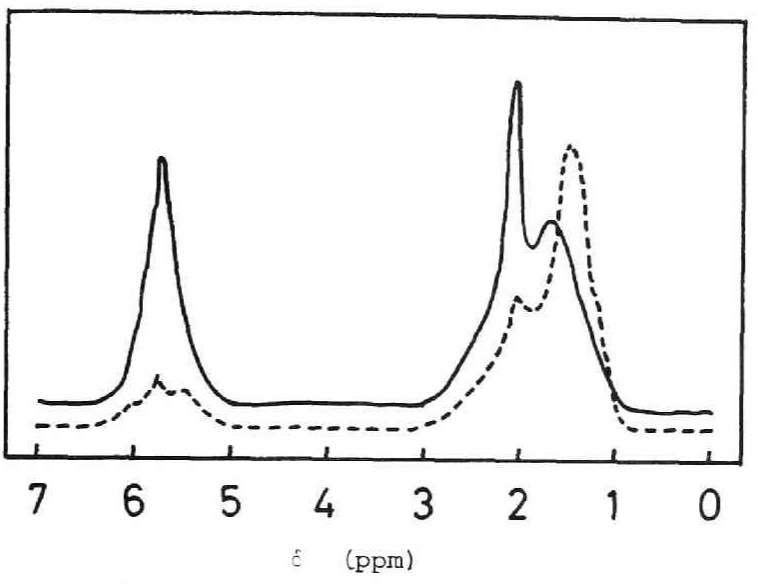

Fig. 4. The NMR spectra of poly-CHPD. (——); n-BnLi, tetrahydrofuran, room temperature. (-----); $SnCl_4$-TCA, methylene chloride, 0°C.
Tetramethyl silame was used as internal standard.

II. With regard to the polymers produced with cationic initiators, NMR and IR spectra showed the presence of olefinic protons (the structures I and II), and UV spectra indicated the presence of the structure III (conjugated double bonds are possible for this structure). The amount of double bond determined by the bromination was higher than that by NMR analysis. This support the presence of the structure III. At the same time the amount of olefinic protons determined by NMR spectroscopy and the amount

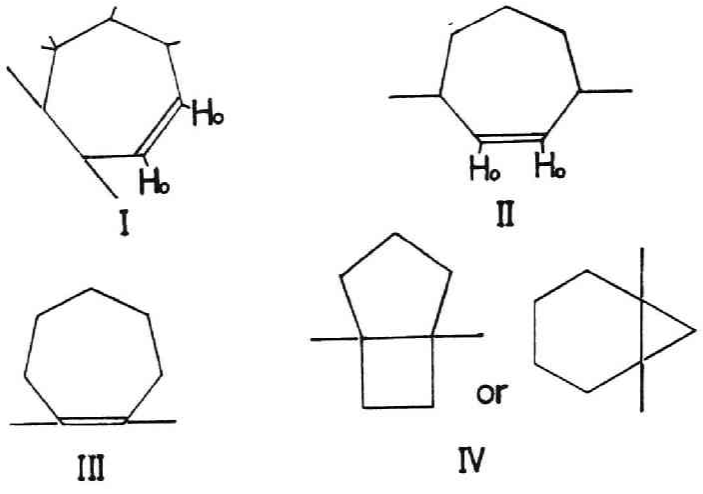

Fig. 5. Proposed structures for poly-CHPD.

of double bond determined by bromination indicated the presence of the saturated monomer unit, which suggests the structure IV. Therefore, all the structural units I, II, III and IV take part in the polymer obtained in the cationic polymerization. To explain the scarcity of olefinic protons structures similar to III and IV have been proposed previously. The structure III is analogous to the structure of polycyclopentadiene produced by the hydrogen-migration mechanism.[9] Similarly, Marvel et al.[10] reported the saturated structure of poly-1,5-cycloöctadiene analogous to the structure IV. This structure could have resulted from the transannular polymerization. In the present polymers, the details of the structures III and IV are not clear. If they are acceptable, the hydrogen-transfer polymerization and the transannular polymerization should occur simultaneously in the cationic polymerization of CHPD. Thus the polycycloheptadiene produced in the cationic polymerization must have a very

complicated structure composed of at least four kinds of monomer units shown in Figure 5.

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Chapter 4

1,3-Cycloöctadiene

INTRODUCTION

A series of investigations have been made on the cationic polymerization of cyclic dienes. In paticular, cyclopentadiene (CPD) has been investigated in detail.[1,2] Also the polymerizations of 1,3-cyclohexadiene (CHXD)[3] and of 1,3-cycloheptadiene (CHPD)[4] were studied. All these monomers were the cyclic dienes of normal-membered ring, and many interesting aspects have been encountered with these monomers, which have not been observed with other vinyl monomers.

The investigation of the effect of the ring size on the polymerization of cyclic dienes will help to elucidate the behaviour of cyclic dienes in cationic polymerization. In this connection, cis,cis-1,3-cycloöctadiene (COD), which is a cyclic diene with a medium-membered ring, was chosen as the next monomer to investigate. The kinetic features in the polymerization of COD are reported and discussed in this chapter in comparison with those of CPD.

EXPERIMENTAL

Materials

COD can assume two types of configurations, i.e., cis, cis and

cis, trans. Commercially available COD was used in this investigation. The infrared spectrum of COD showed absorptions at 11.0 and 8.65 μ,[5] the nuclear magnetic resonance spectrum (NMR) showed peaks at τ=4.45, 7.90, and 8.60 ppm,[5] and n_D^{20} was 1.4938.[5] All these physical values indicate that the present COD assumes a cis,cis configuration.

COD was distilled twice from calcium hydride through packed column under nitrogen stream (b.p. 75.0°C/100 mmHg). The purity of COD checked by gas chromatography was higher than 99.9 %.

Toluene and methylene chloride, as solvent, and titanium tetrachloride ($TiCl_4$), as catalyst, were purified as described in earlier chapters. Trichloroacetic acid (TCA) was used without further purification as cocatalyst.

Procedure

All polymerizations were carried out at -78°C using an equimolar mixture of $TiCl_4$ and TCA as a catalyst. The polymerization procedure was almost the same as described in earlier chapters. The conversion of monomer was determined by the weight of methanol-insoluble polymer formed. The water content of the polymerization system was determined by the Karl Fischer method.

The molecular weight of polymer was determined by ebulliometer. Intrinsic viscosities of toluene solution were also measured at 30°C.

RESULTS

In all systems studied, the polymerization started immediately

upon addition of the catalyst. The polymerization solution was not completely homogeneous and was coloured red, but the purified polymer was white. Very little methanol-soluble product was formed.

1. Effect of Catalyst Concentration.

The time-conversion curves for the polymerizations catalyzed by $TiCl_4$-TCA in toluene and in methylene chloride are shown in Figures 1 and 2, respectively.

As is seen in Figure 1, the polymerization in toluene is very fast at first but slows down toward the end. The same situation has been encountered in the polymerization of CPD initiated by $SnCl_4$-TCA in toluene at -78°C.[2)]

Figure 2 shows that the polymerization in methylene chloride is faster at first than that in toluene, but that it almost completely stops before it goes to completion. The same situation has been encountered in the polymerization of CPD initiated by $TiCl_4$-TCA in toluene at -78°C.[1)]

It should be noted here that the polymerization rate of CPD is larger than that of COD, as judged by the comparison on the time-conversion curves in toluene at -78°C.[1)] On the other hand, the polymerization of CHXD by $TiCl_4$-TCA was investigated only at 0°C,[3)] so a precise comparison of the polymerization rate of COD with that of CHXD is difficult. However, the polymerization of CHXD in methylene chloride at -78°C reached a much higher conversion than that of COD even when catalyzed by a less acidic catalyst, $SnCl_4$-TCA, in a smaller concentration.[3)] This would mean that

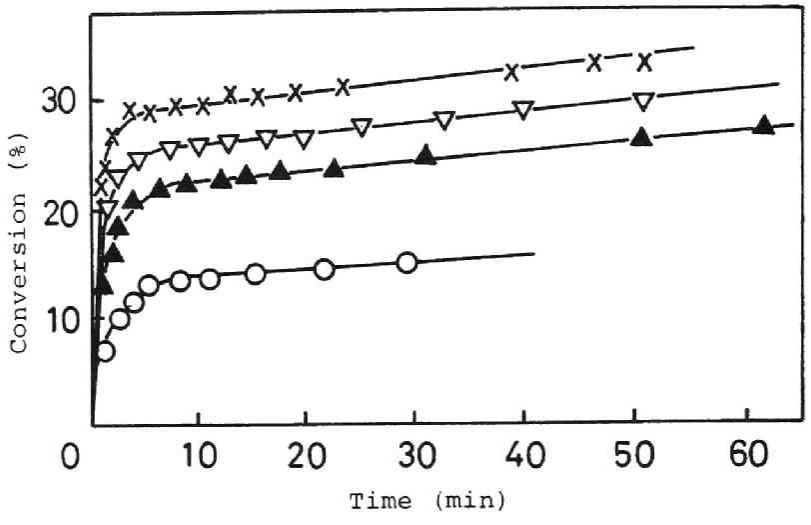

Fig. 1 Time-conversion curves of polymerization of COD catalyzed by $TiCl_4$-TCA in toluene at -78°C. $[M]_o$ 0.73 mole/l. $[C]_o$ X 50 mmole/l, ▽ 45 mmole/l, ▲ 35 mmole/l, ○ 20 mmole/l. $[H_2O]_o$ 2.8 mmole/l.

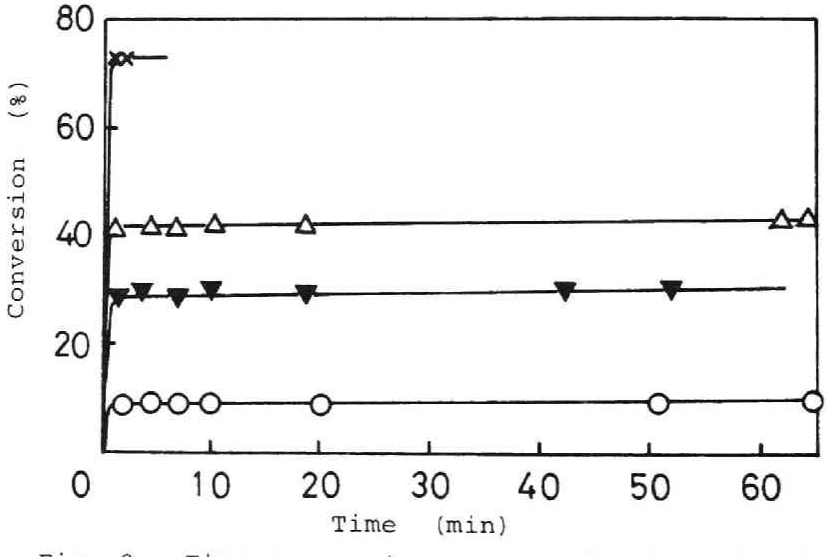

Fig. 2. Time-conversion curves of polymerization of COD catalyzed by $TiCl_4$-TCA in methylene chloride at -78°C. $[M]_o$ 0.73 mole/l. $[C]_o$ X 80 mmole/l, △ 20 mmole/l, ▼ 10 mmole/l, ○ 5.0 mmole/l.

CHXD is polymerized faster than COD in the cationic polymerization. Analogous comparison is possible between COD and CHPD.[4] CHPD seems to be polymerized faster than COD. It follows, therefore, that the reactivity of cyclic dienes in the cationic polymerization decreases as the ring size increases, that is, in the order:

CPD > CHXD > CHPD > COD

As pointed out above, the shape of time-conversion curves of the polymerization of COD in toluene is very similar to that of the polymerization of CPD in toluene initiated by $SnCl_4$-TCA, where the polymerization was explained in terms of the coexistence of the first non-stationary state polymerization and the later stationary state polymerization.[2]

Likewise, the polymerization of COD in toluene initiated by $TiCl_4$-TCA was divided into two parts; that is, the first, fast polymerization and the later, slow polymerization. The intercept given by the extrapolation of time 0 of the time-conversion curve for the later, slow polymerization would represent approximately the final conversion reached by the first, fast polymerization. The effects of initial catalyst concentration $[C]_o$ on the final conversion reached in the fast polymerization and the later, slow polymerization are shown in Figure 3.

Figure 3 shows that the final conversion in the fast polymerization is proportional to $[C]_o$, but that the later, slow polymerization is almost independent of $[C]_o$.

With polymers obtained in toluene, the relationships between the intrinsic viscosity and $[C]_o$, the intrinsic viscosity and the conversion, and the number-average molecular weight and the conversion

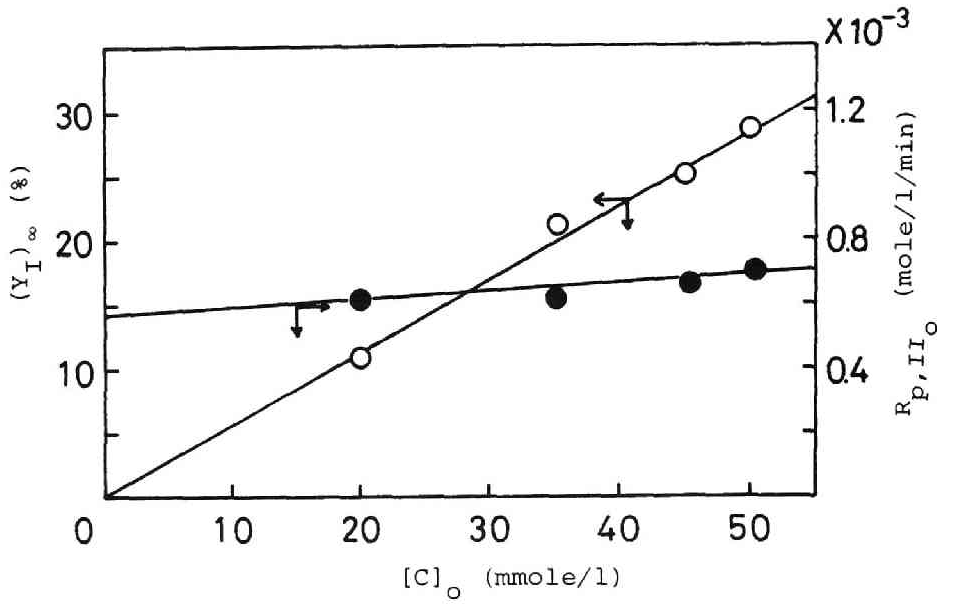

Fig. 3. Effect of initial catalyst concentration on final conversion of first-step polymerization $(Y_I)_\infty$ (○) and initial rate of second-step polymerization R_{p,II_o} (●). Conditions the same as in Fig. 1.

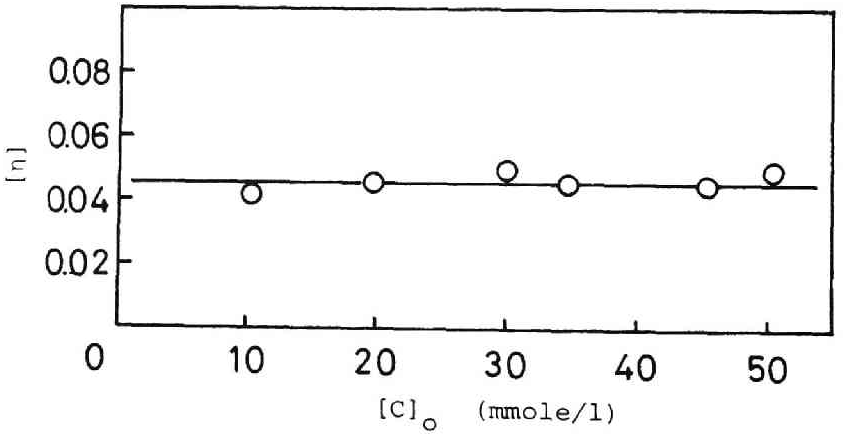

Fig. 4. Relationship between initial catalyst concentration $[C]_o$ and [η] of polymer obtained by $TiCl_4$-TCA in toluene at -78°C. Conditions the same as in Fig. 1.

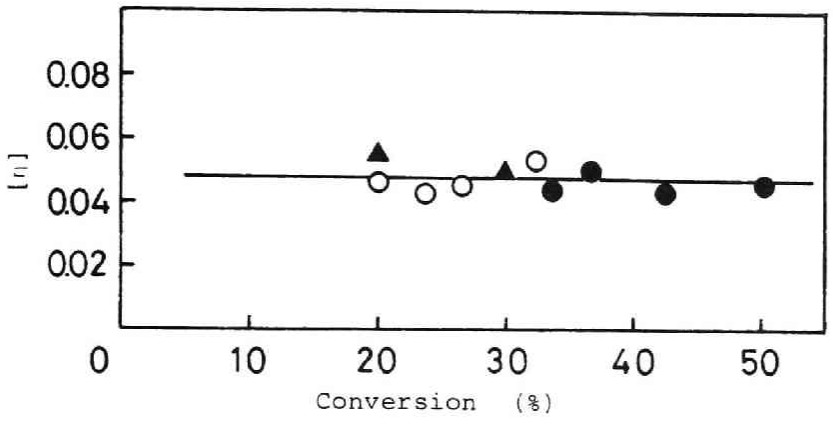

Fig. 5. Relationship between conversion and [η] of polymer obtained by $TiCl_4$-TCA in toluene at -78°C. $[M]_o$ 0.73 mole/l. $[C]_o$ ▲ 30 mmole/l, ○ 35 mmole/l, ● 50 mmole/l.

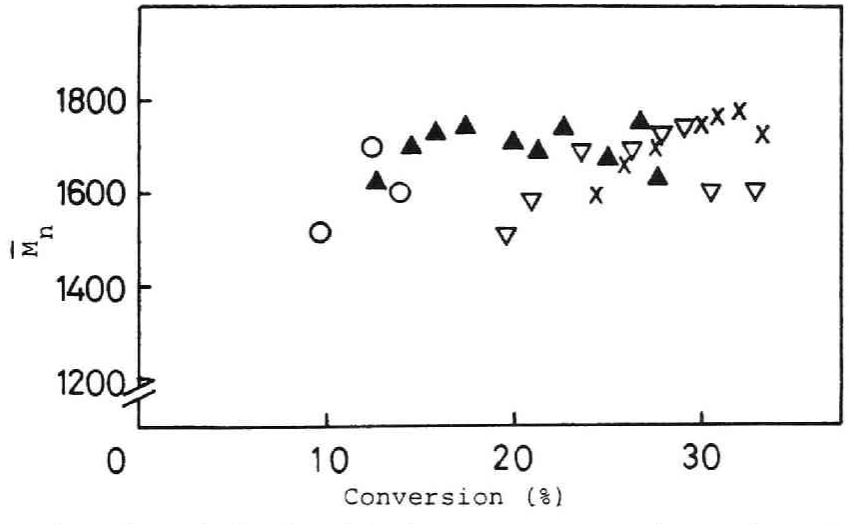

Fig. 6. Relationship between conversion and number-average molecular weight of polymer obtained by $TiCl_4$-TCA in toluene at -78°C. Conditions the same as in Fig.1.

were investigated. The results are shown in Figures 4-6. The number-average molecular weights of polymers produced in toluene were found to range 1500 to 1800 and were almost unaffected by the changes of $[C]_o$ and conversion. This is in contrast to the fact that the intrinsic viscosity of polycyclopentadiene produced in toluene by $TiCl_4$-TCA or $SnCl_4$-TCA decreased with $[C]_o$.[1,2]

The dependence on $[C]_o$ of the intrinsic viscosity of polycyclooctadiene obtained in methylene chloride by $TiCl_4$-TCA is shown in Figure 7. The intrinsic viscosity seems to increase only slightly with increasing $[C]_o$.

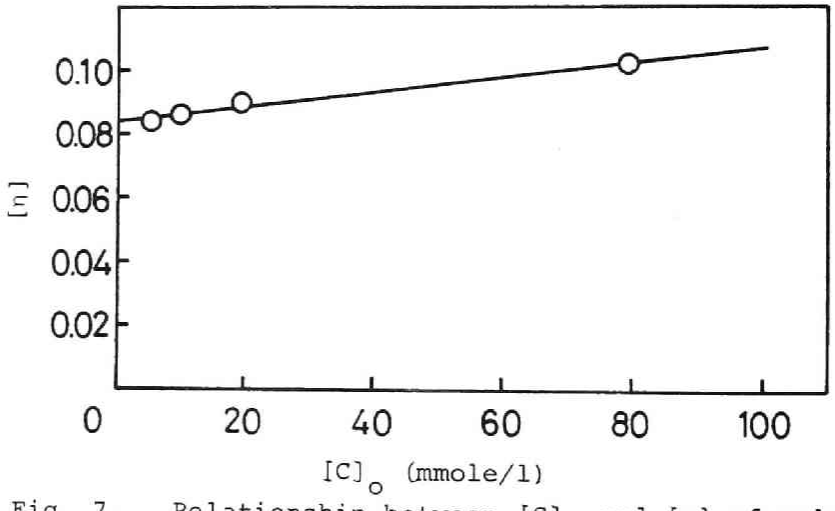

Fig. 7. Relationship between $[C]_o$ and $[\eta]$ of polymer obtained by $TiCl_4$-TCA in methylene chloride at -78°C. Conditions the same as in Fig. 2.

2. Effect of Monomer Concentration.

Polymerizations were carried out in toluene by $TiCl_4$-TCA at various initial monomer concentrations ($[M]_o$). The time-conversion curves are shown in Figure 8. Similarly to the case shown in Figure 1, the time-conversion curve was divided into two stages regardless

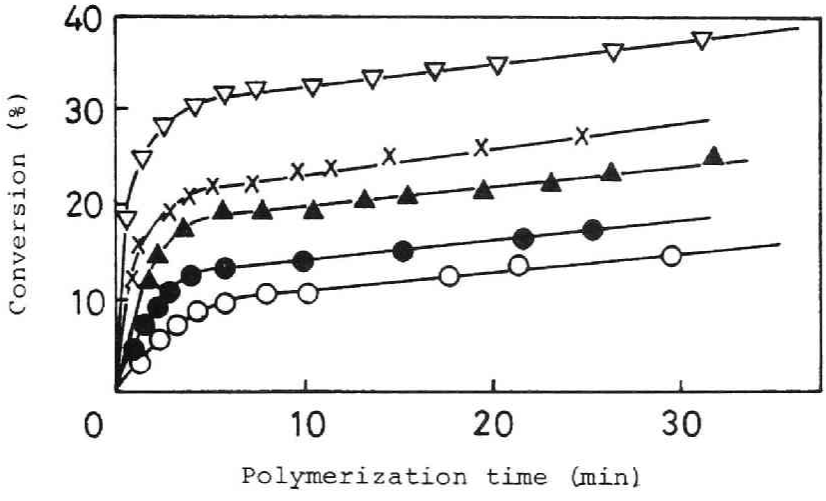

Fig. 8. Time-conversion curves of polymerization of COD catalyzed by $TiCl_4$-TCA in toluene at -78°C. $[M]_o$; ▽ 0.365 mole/l, X 0.548 mole/l, △ 0.73 mole/l, ● 0.913 mole/l, ○ 1.10 mole/l. $[C]_o$ 33.6 mmole/l. $[H_2O]_o$ 2.3-2.4 mmole/l.

of $[M]_o$; that is, the first, fast polymerization and the later, slow polymerization. The effects of $[M]_o$ on the final conversion of the fast polymerization and on the rate of the slow polymerization were investigated and are shown in Figure 9.

As can be seen in Figure 9, the rate of the slow polymerization was proportional to $[M]_o$. On the other hand, the final conversion of the fast polymerization decreased as $[M]_o$ increased. This inversion phenomenon has been found in some cases, e.g., CPD–$TiCl_4$-TCA–toluene,[1] CHD–$SnCl_4$-TCA–benzene, methylene chloride systems.[3] However, it should be noted in Figure 9 that the amount of monomer consumed (conversion times $[M]_o$,mole/l) during the fast polymerization is almost unchanged with variation of $[M]_o$. Since

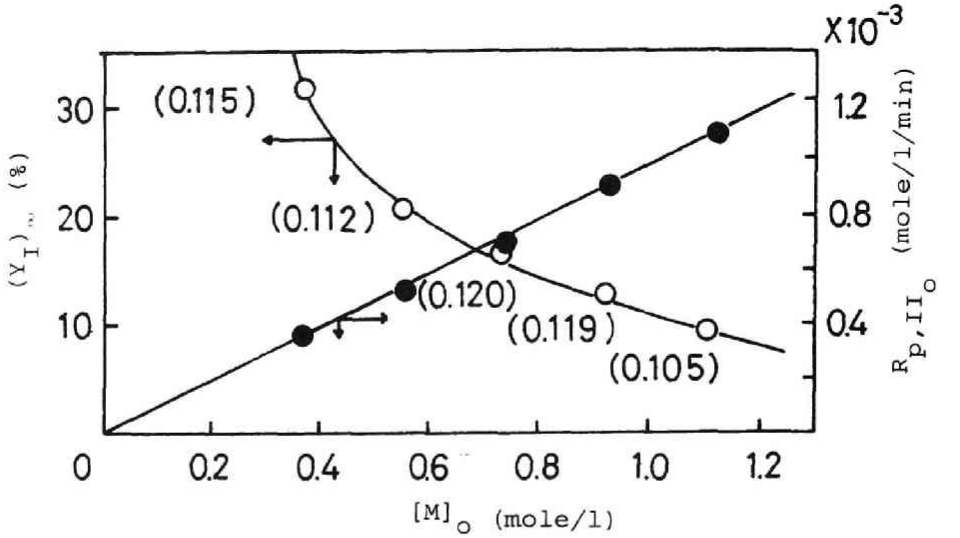

Fig. 9. Effect of initial monomer concentration on final conversion of first-step polymerization (Y_I) (○) and initial rate of second-step polymerization R_{p,II_o} (●). Conditions the same as in Fig. 8. Figures in parentheses represent the amount of monomer consumed (mole/liter) during first-step polymerization.

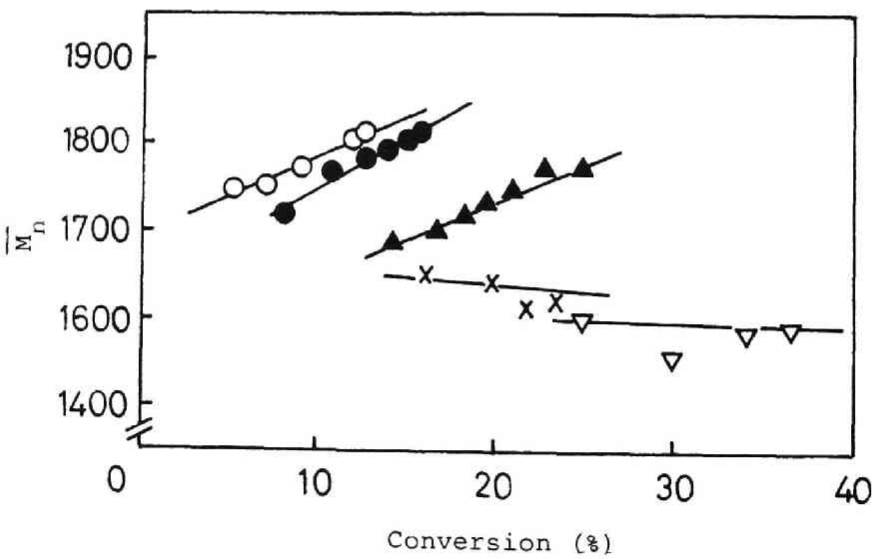

Fig. 10. Relationship between conversion and number-average molecular weight of polymer obtained by $TiCl_4$-TCA in toluene at -78°C. Conditions the same as in Fig. 8.

the fast polymerization lasts for about 5 min regardless of $[M]_o$ (cf. Figure 8), the polymerization rate (mole/l/min) of the fast polymerization is nearly independent of $[M]_o$.

The effect of $[M]_o$ on the number-average molecular weight of polymer was investigated. As seen in Figure 10, the polymer molecular weight increased a little as $[M]_o$ increased. When $[M]_o$ was larger than 0.73 mole/l, the polymer molecular weight tended to increase with increasing conversion.

DISCUSSION

The rate behavior is discussed here, particularly in connection with initiation mechanism.

As stated above, the polymerization in toluene was divided into two steps. The initial rate of the first step is represented by R_{p,I_o} and that of the second step by R_{p,II_o}. The kinetic investigations above are summarized in the following equations:

$$R_{p,I_o} = K_I \cdot [C]_o^{1.0} \cdot [M]_o^{0} \qquad \text{non-stationary state} \qquad (1)$$

$$R_{p,II_o} = K_{II} \cdot [C]_o^{0} \cdot [M]_o^{1.0} \qquad \text{possibly stationary state} \qquad (2)$$

where K_I and K_{II} represent the overall rate constant for each step, the subscript o represents the initial concentration, and the superscript represents the kinetic order.

A strong interaction between metal halide and monomer, and a catalyst inactivation by a reaction having higher order with respect to monomer concentration, have been observed in the cationic polymerizations of CPD,[1,2] and CHXD,[3] and seem to be common with other

cyclic dienes. The same idea was incorporated into the kinetic interpretation of the present results.

A strongly electrophilic $TiCl_4$(C) reacts quickly with a nucleophilic COD (M) to form a complex (MC).

$$M + C \xrightarrow{fast} MC \tag{3}$$

In view of much higher concentration of monomer than catalyst,

$$[MC]_o \equiv [C]_o \tag{4}$$

At the beginning of the polymerization no stationary state about MC is established, but TCA (Co) and COD compete for MC, leading the formation of active species of polymerization (P*) and inactive complex (M_2C).

$$M_2C \xleftarrow{+M,k_1} MC \xrightarrow{+Co,k_2} P^* \tag{5}$$

Therefore,

$$[P^*]_o = \frac{k_2[Co]_o[C]_o}{k_1[M]_o + k_2[Co]_o} \tag{6}$$

Thus,

$$R_{p,I_o} = \frac{k_p . k_2[C]_o[Co]_o[M]_o}{k_1[M]_o + k_2[Co]_o} \tag{7}$$

where k_p represents the propagation rate constant. The effects of $[M]_o$ and $[Co]_o$ on $R_{p,I}$ may be of minor importance. Thus, Eq. (7) coincides with Eq. (1) qualitatively.

When the fast polymerization induced by the initially formed complex MC is finished, the polymerizations are carried out by the complex MC formed by a slow decomposition of the complex M_2C.

$$M_2C \xrightarrow[\text{slow}]{k_3} M + MC \xrightarrow[\text{fast}]{+Co,\,k_2} P^* \qquad (8)$$

The initial concentration of M_2C is

$$[M_2C]_o = \frac{k_1[M]_o[C]_o}{k_1[M]_o + k_2[Co]_o} \qquad (9)$$

Then the rate of initiation is

$$R_{i_o} = k_3[M_2C]_o = \frac{k_1 \cdot k_3[M]_o[C]_o}{k_1[M]_o + k_2[Co]_o} \qquad (10)$$

If the unimolecular termination reaction occurs, and the stationary concentration of P* is established,

$$R_i = R_t = k_t[P^*] \qquad (11)$$

$$[P^*] = \frac{k_1 \cdot k_3}{k_t} \cdot \frac{[M]_o[C]_o}{k_1[M]_o + k_2[Co]_o} \qquad (12)$$

Thus,

$$R_{p,II_o} = \frac{k_p \cdot k_1 \cdot k_3}{k_t} \cdot \frac{[M]_o^2[C]_o}{k_1[M]_o + k_2[Co]_o} \qquad (13)$$

Since $[C]_o = [Co]_o$ always, R_{p,II_o} would be almost unaffected by $[C]_o$. Equation (13) is in qualitative agreement with Eq. (2).

The second-stage polymerization was not observed in methylene chloride. This may be because the decomposition of the complex M_2C is unfavored in methylene chloride. In CPD–$TiCl_4$-TCA system,[1] the second-stage polymerization was not observed even in toluene. In view of much stronger nucleophilicity of CPD than COD, the decomposition of $(CPD)_2$-$TiCl_4$ complex would be highly prohibited.

The molecular weight of polycycloöctadiene was low, while the polymerization rate was quite high. This would mean that the monomer transfer reaction predonominates over other chain-breaking reactions.

As stated above, the fast initiation reaction and the catalyst deactivation by excess monomers, which are based on the strong interactions between a metal halide and a cyclic diene, were common to CPD, CHXD, and COD. But the reactivation of cyclic diene, metal halide adduct to give an initiating species was suggested first with COD. On that basis, the kinetic observations were interpreted.

The present investigation showed that the reactivity of cyclic dienes decreased in the order, CPD > CHXD > CHPD > COD. Clearly, they are in the sequence of increasing steric interference. It is reasonable to assume that the reactivity of cyclic dienes is governed by the steric factor. This point will be further discussed in Chapter 7. The stability of cycloalkenyl cations may be another important factor in determining the reactivity of dienes, as suggested in the previous chapters. However, no data are available concerning the stability of cycloöctenyl cation. In this connection, more research on the properties of cycloöctenyl cation is desirable.

References

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PART II

COPOLYMERIZATION STUDIES

OF CYCLYC DIENES

Chapter 5

Copolymerization of Cyclopentadiene with α-Methylstyrene

INTRODUCTION

The cationic polymerization of a series of conjugated cyclic dienes (5–8-membered rings) was presented in Part I. Among these, cyclopentadiene (CPD) shows particularly high reactivity toward cationic catalysts. In the present chapter, the reactivity of CPD was compared with that of α-methylstyrene (α-MS), which was a rather reactive monomer among styrene derivatives in cationic polymerization.

Monomer reactivity ratios were determined in a few solvents of different polarity, as the solvent effect on the monomer reactivity ratio in the cationic copolymerization has been a subject of current interest. It has been reported that although the solvent effect is not marked in the copolymerization between styrene derivatives,[1] it is quite important in the copolymerization between structurally dissimilar monomers such as isobutene–styrene,[2,3] styrene–alkyl vinyl ether,[4] and CPD–isobutene.[5] So the study of copolymerization of CPD with α-MS will help to solve the problem on the relationship between the structure and the reactivity of cyclic dienes.

EXPERIMENTAL

Procedure

In a 100 ml flask flashed with nitrogen, known amounts of solvent and monomer were charged with a syringe through a self-sealing rubber cap. The flask was chilled in liquid nitrogen and the air in the flask was completely exchanged with nitrogen under vacuum manipulation. Thereafter the flask was transferred into a dry ice–methanol bath and after a thermal equilibrium was reached the catalyst solution was added with a syringe to initiate the copolymerization. After a suitable time for the conversion not to exceed 20 %, methanol was added to stop the copolymerization. When the copolymerization is conducted in n-hexane, a precooled monomer mixture was added to a mixture of solvent and catalyst because the polymer is insoluble. The copolymer was washed with methanol repeatedly and dried in vacuum. As polycyclopentadiene (PCPD) is known to be oxidized quickly,[6] 4,4'-thiobis(6-t-butyl-3-methylphenol) was used as an antioxidant to avoid the oxidation of copolymer.

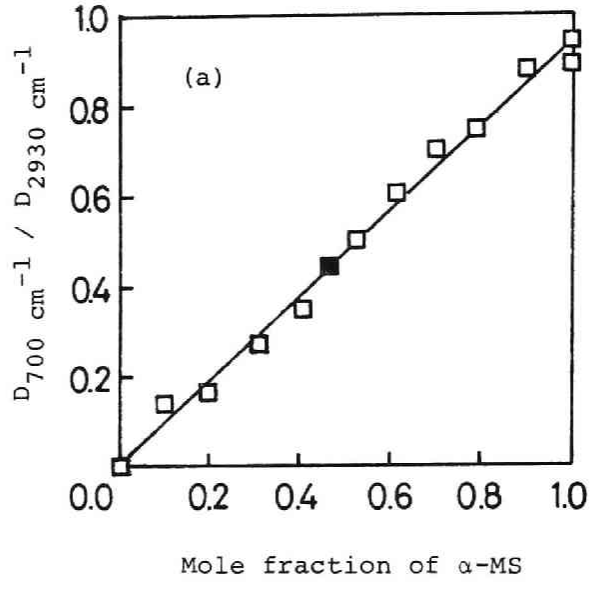
Analysis of Copolymer Composition

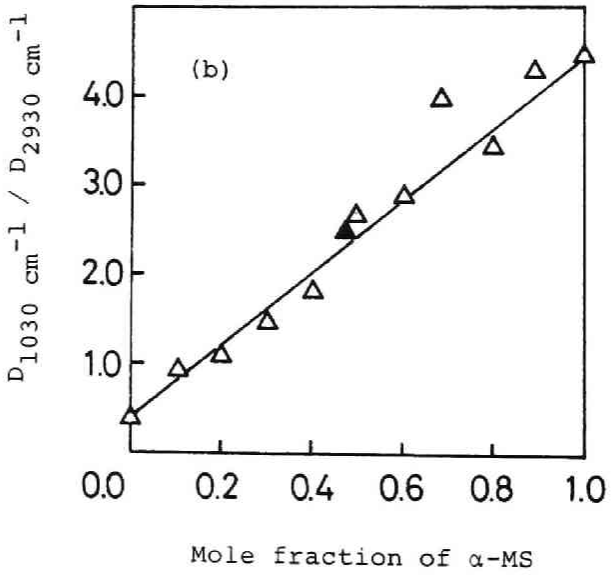
The elementary composition of poly-α-methylstyrene (P-α-MS, C % 91.53) is very similar to that of PCPD (C % 90.91). Hence the elementary analysis for copolymer composition is not suitable. The copolymer composition was analyzed by infrared (IR) spectroscopy, as will be described subsequently. The IR spectra of

P-α-MS and PCPD were measured as carbon disulfide solution or potassium bromide disk. An absorption at 2930 cm^{-1} due to a methylene group appeared in both polymers. Two absorptions at 1030 and 700 cm^{-1} due to a phenyl group appeared only in P-α-MS. These three absorption bands were employed as key band to analyze the copolymer composition.

The mixtures of P-α-MS and PCPD of various molar compositions were made and their IR spectra were measured as 2.5 % carbon disulfide solution or as potassium bromide disk. The optical density ratios $D_{1030\ cm^{-1}}/D_{2930\ cm^{-1}}$ and $D_{700\ cm^{-1}}/D_{2930\ cm^{-1}}$ are calculated and plotted in Figure 1 as a function of the mole fraction of α-MS in the polymer mixture. Straight lines were obtained and these were used as calibration lines for the analysis of copolymer composition. In this procedure an assumption was made that the molar extinction coefficient of a key band of copolymer is the same as that of the polymer mixture. To support the assumption, a mixture of α-MS (mole fraction 0.471) and CPD (mole fraction 0.529) was copolymerized up to 100 % conversion. The resultant copolymer was subjected to IR spectroscopy. If the assumption is correct, the copolymer composition analyzed by IR spectroscopy should be equal to the composition of the feed monomer, and this was the case. The results of the test experiment are shown in Figure 1 as black points. They very nearly form the straight lines.

With methods (a) and (b) the compositions of copolymers produced in toluene were analyzed at different concentrations in carbon disulfide solution (2.5 and 5 %). The change in concentration was found not to affect the determination.


(a)
1.0
0.8
0.6
0.4
0.2
0.0
0.2
0.4
0.6
0.8
1.0
$D_{700\ cm^{-1}} / D_{2930\ cm^{-1}}$
Mole fraction of α-MS


(b)
4.0
3.0
2.0
1.0
0.0
0.2
0.4
0.6
0.8
1.0
$D_{1030\ cm^{-1}} / D_{2930\ cm^{-1}}$
Mole fraction of α-MS

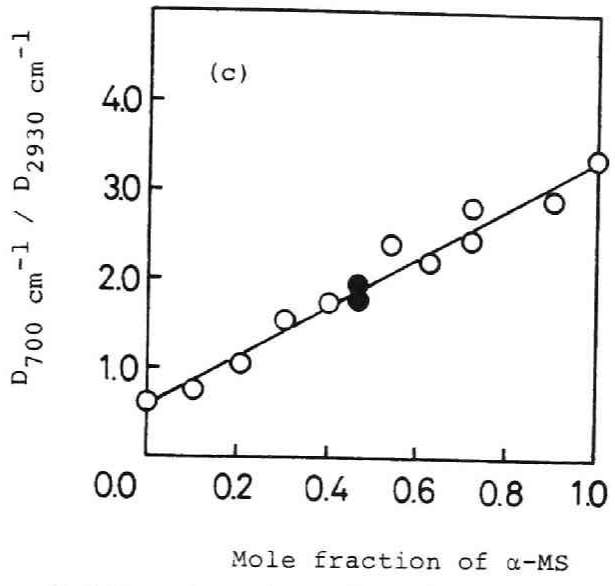


Fig. 1. Calibration lines for the determination of copolymer composition. (a) CS_2 solution, $D_{1030\ cm^{-1}} / D_{2930\ cm^{-1}}$ vs.mole fraction of α-MS; (b) CS_2 solution, $D_{700\ cm^{-1}} / D_{2930\ cm^{-1}}$ vs.mole fraction of α-MS; (c) KBr disk, $D_{700\ cm^{-1}} / D_{2930\ cm^{-1}}$ vs. mole fraction of α-MS.

The compositions of three copolymers were analyzed by nuclear magnetic resonance (NMR) spectroscopy as well as IR spectroscopy. The results are compared in Table I. It is seen that the analyses are in fairly good agreement. Thus the validity of the use of IR spectroscopy was again revealed.

TABLE I

Analyses of Copolymer Composition by IR Spectroscopy and NMR Spectroscopy

Sample	F_1[a] by IR (mean value)	F_1[a] by NMR (integral curve)	F_1[a] by NMR (area ratio of phenyl proton)
A	0.470	0.473	0.494
B	0.886	0.921	0.962
C	0.322	0.535	0.417

[a] F_1, mole fraction of α-MS in copolymer.

Identification of the True Copolymerization

To identify that the true copolymerization took place, fractionation of the copolymerization product was carried out. About a 1 % toluene solution of the copolymerization product was made, and a small amount of methanol as a precipitant was added successively. The copolymerization product was divided into five fractions, and with each fraction the compsition and the viscosity were measured. Some low molecular weight fraction was lost, mainly during the process of filtration. As is seen in Table II, in going from fraction 1 to fraction 5, the intrinsic viscosity decreases but the copolymer composition was almost unchanged.

Next, the homopolymers of α-MS and CPD were produced under the same conditions as the copolymerization, and they are mixed and fractionated in the way as described above. The results are

TABLE II

Fractionation of Copolymerization Product[a]

Fraction	Weight %	[η], dl/g	F_1[b]
Original		0.399	0.385
1	18.9	0.699	0.396
2	16.0	0.496	0.375
3	16.3	0.432	0.427
4	10.5	0.161	0.452
5	3.7	——	0.436

[a] Copolymerization condition; solvent toluene, catalyst $BF_3 \cdot O(C_2H_5)_2$, temperature -78°C.

[b] Mole fraction of α-MS in copolymer.

shown in Table III. In going from fraction 1 to fraction 5 the intrinsic viscosity decreased but F_1 increased. This is because the low molecular weight P-α-MS precipitates later. Hence, if P-α-MS is formed at all in the copolymerization condition, it should come out later, when fractionated. This was not observed actually, and the formation of true copolymer was confirmed.

Viscosity

The viscosity of copolymer was measured in toluene solution at 30°C.

TABLE III

Fractionation of the Mixture of P-α-MS and PCPD

Fraction	Weight %	[η], dl/g	F_1 [b]
Original		0.716	0.440
1	11.2	1.451	0.098
2	6.48	1.325	0.173
3	15.1	0.594	0.293
4	25.7	0.501	0.555
5	6.57	0.150	0.578

[a] Polymerization condition; solvent toluene, catalyst $BF_3 \cdot O(C_2H_5)_2$, temperature -78°C.

[b] Mole fraction of α-MS in copolymer.

Materials

α-MS was washed with 10 % aqueous sodium hydroxide solution, dried over anhydrous potassium carbonate, and distilled under reduced pressure twice.

n-Hexane (guaranteed reagent) was shaken with concentrated sulfuric acid, water, sodium hydroxide solution, alkaline potassium permanganate solution, and water, dried over calcium chloride, and distilled from metallic sodium.

Purifications of the other reagents were described in earlier chapters.

RESULTS

The copolymerizations of α-MS (M_1) and CPD (M_2) were carried out in methylene chloride, toluene, or n-hexane as solvent with boron trifluoride etherate as catalyst. All copolymerizations were carried out at -78°C with the initial total monomer concentration 20 vol % and the initial catalyst concentration 50 mmole/l.

TABLE IV

Analysis of the Composition of Copolymer Obtained in Methylene Chloride

Run No.	f_1	F_1			
		Method (a)	Method (b)	Method (c)	Mean
200	0.000	0.000	0.000	0.000	0.000
201	0.060	——	0.0268	0.0484	0.0376
202	0.126	0.102	0.0945	0.0550	0.0838
203]	0.198	——	——	0.159 0.131	0.145
204	0.276	——	0.177	0.215 0.176	0.189
205	0.366	0.306	0.306	0.264 0.291	0.292
206	0.471	0.348	0.400	0.296 0.330	0.344
207	0.571	0.507	0.548	0.465 0.464	0.496
208	0.697	0.547	0.682	0.558	0.596
209	0.839	0.780	——	0.780	0.780
210	1.000	1.000	1.000	1.000	1.000

1. Copolymer Composition.

The copolymer composition was analyzed by IR spectroscopy as potassium bromide disk or as carbon disulfide solution. The monomer reactivity ratios were determined by the cross-section method.

The analysis of copolymer composition produced in methylene chloride is shown in Table IV. The mole fraction of α-MS in copolymer (F_1) was determined by averaging three F_1 values determined by three differnt ways.

The compositions of copolymers obtained in methylene chloride, toluene, and n-hexane were plotted as a function of the fraction of α-MS in the monomer feed in Figures 2, 3, and 4, respectively.

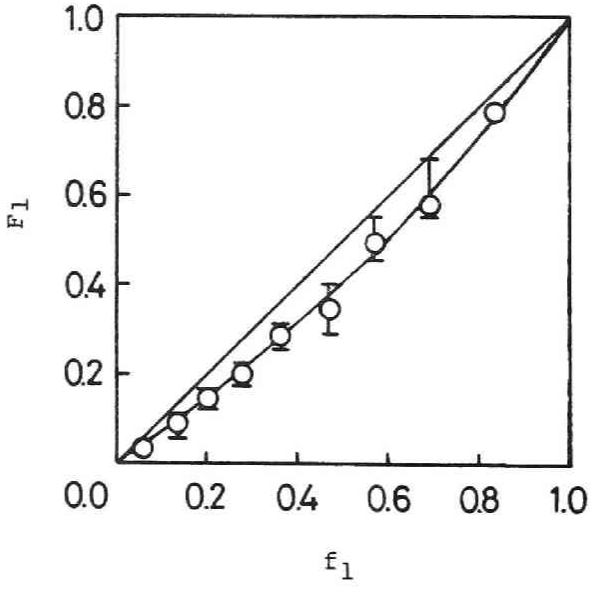


Fig. 2. Copolymer composition curve. Copolymerization of α-MS(M_1) and CPD(M_2) in methylene chloride.

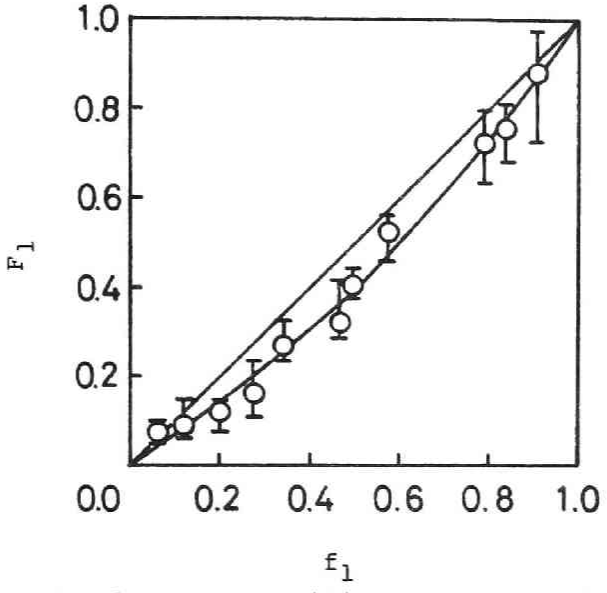


Fig. 3. Copolymer composition curve. Copolymerization of α-MS(M_1) and CPD(M_2) in toluene.

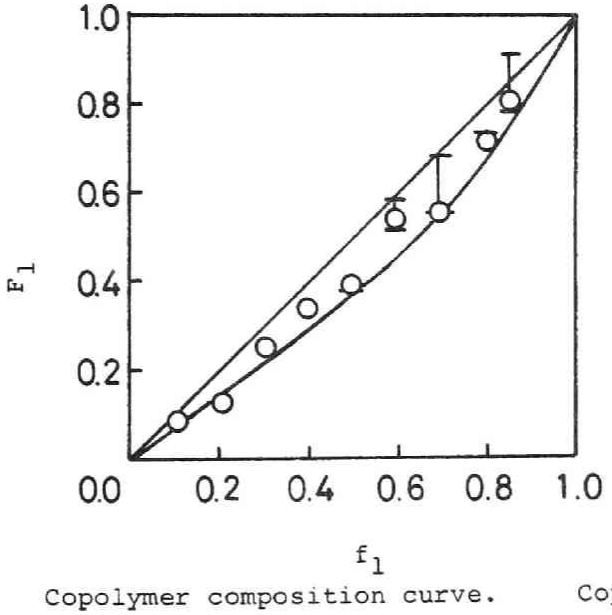


Fig. 4. Copolymer composition curve. Copolymerization of α-MS(M_1) and CPD(M_2) in n-hexane.

The limit of variation in F_1 is also shown in the figures. The copolymer composition curves in the figures correspond to the monomer reactivity ratios determined by the cross-section method using mean values of F_1: $r_1 = 0.67 \pm 0.29$, $r_2 = 1.53 \pm 0.18$ in methylene chloride; $r_1 = 0.66 \pm 0.25$, $r_2 = 1.62 \pm 0.36$ in toluene; $r_1 = 0.47 \pm 0.27$, $r_2 = 1.23 \pm 0.22$ in n-hexane.

2. Viscosity of copolymer.

The intrinsic viscosities of the copolymers were measured in toluene solution at 30°C and is shown in Figure 5 as a function of f_1. The CPD rich copolymers produced in methylene chloride and in n-hexane were not completely soluble in toluene. It was

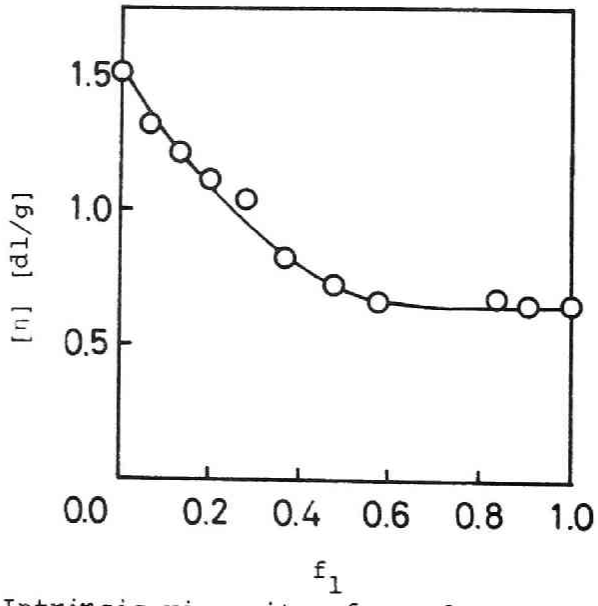


Fig. 5. Intrinsic viscosity of copolymer and composition of feed monomer. Copolymerization of α-MS(M_1) and CPD(M_2) in toluene.

found that the copolymerization in toluene yielded copolymers, the intrinsic viscosities of which were higher than or near unity. In the copolymerizations in n-hexane and in methylene chloride the intrinsic viscosity of copolymer tended to decrease with increasing α-MS content in the feed monomer. It is of particular interest that the viscosity of copolymer was not extremely lower than those of homopolymers, because a very marked decrease of copolymer viscosity was observed with isobutene–styrene[7] or α-MS[8] copolymerization.

3. Oxidation of Copolymer.

The autooxidation of α-MS–CPD copolymer was investigated by IR spectroscopy. It has been known that PCPD is oxidized by air very rapidly, and that with oxidation the IR absorption due to a carbonyl group at 1700 cm^{-1} increases its intensity but the absorption due to a double bond at 3050 cm^{-1} is unchanged.[6] The change of the IR spectrum of the film of the α-MS–CPD copolymer on standing in air is shown in Figure 6. The ratio of optical density D_{1700} cm^{-1}/D_{3050} cm^{-1} was calculated and its variation with time was recorded with several samples in Table V. It was found that oxidation by air can be avoided by the addition of antioxidant, and that the copolymer, which contains more α-MS, is oxidized more slowly.

DISCUSSION

The cationic copolymerizations of α-MS and CPD were carried out and the monomer reactivity ratios were determined. It was

TABLE V

Oxidation Rate of the Film of α-MS (M_1)—CPD (M_2) Copolymer[a]

Sample		Time, days	D_{1700} cm^{-1}/D_{3050} cm^{-1}
No. 1, F_1 = 0.06	Without antioxidant	0	0.10
		11	0.31
		32	0.66
		49	0.89
		108	1.17
	With antioxidant	0	0.13
		7	0.13
		15	0.14
		28	0.14
		45	0.15
		104	0.14
No. 2, F_1 = 0.49	Without antioxidant	0	0.07
		7	0.06
		28	0.11
		45	0.12
		104	0.13
	With antioxidant	0	0.02
		7	0.04
		28	0.02
		45	0.02
		104	0.04

[a] Copolymerization condition; solvent toluene, catalyst $BF_3 \cdot O(C_2H_5)_2$, temperature -78°C.

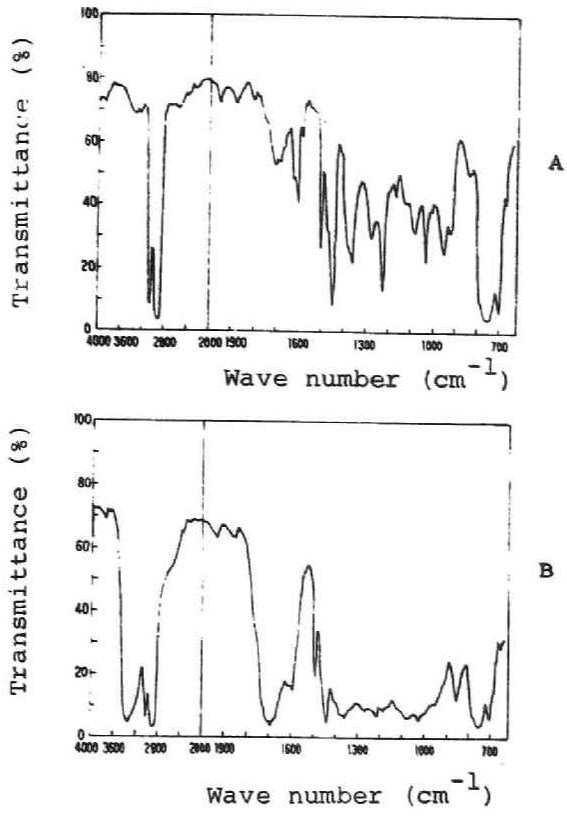


Fig. 6. Change of IR spectrum of α-MS–CPD copolymer on oxidation. Copolymer produced in toluene with $BF_3 \cdot O(C_2H_5)_2$ at -78°C. F_1 = 0.06. A soon after a film was cast; B after 108 days.

found that CPD was more reactive than α-MS, and that the effect of solvent polarity on the monomer reactivity ratio was small.

The monomer reactivity ratios for the copolymerizations of CPD so far obtained are listed in Table VI. It is seen that the effect of solvent polarity on the monomer reactivity ratio is more important in isobutene–CPD than in α-MS–CPD.

In cationic polymerization the reactivity of monomer may be determined by either the nucleophilicity of the double bond or the stability of the resulting cation. The nucleophilicity of

TABLE VI

Copolymerization of CPD

M_1	M_2	r_1	r_2	Solvent	Catalyst	Solvent effect	Ref.
Isobutene	CPD	0.60	4.5	toluene	$BF_3 \cdot OEt_2$	large	5
		0.73	1.86	CH_2Cl_2			
		0.21	0.3	toluene	$SnCl_4$-TCA[a]		
		0.80	1.55	CH_2Cl_2			
α-MS	CPD	0.47	1.23	n-hexane	$BF_3 \cdot OEt_2$	little	present chapter
		0.66	1.62	toluene			
		0.67	1.53	CH_2Cl_2			

[a] Trichloroacetic acid.

the double bond may not be affected significantly by the nature of solvent. On the other hand, the stability of the resulting cation is strongly affected by the nature of solvent. An aliphatic cation such as t-butyl cation from isobutene is least resonance-stabilized. It will be quite unstable in a nonpolar solvent such as n-hexane, but will gain a lot of solvation stabilization in a polar solvent such as methylene chloride. On the other hand, an arylic cation such as 1-phenyl ethyl cation from styrene is highly resonance-stabilized. It will be stable even in a nonpolar solvent such as n-hexane, and will not gain as much stabilization energy in a polar solvent. In this respect, the reactivity of aliphatic

olefins will be affected very much by the solvent polarity, and that of arylic olefins will be affected only a little. It follows that the increase of solvent polarity results in a greater increase of the reactivity of the monomer, which gives a less stable ion. On this basis, a large solvent effect on the isobutene-styrene copolymerization and a small solvent effect on the copolymerization between styrene derivatives have been interpreted.[3)]

Turning to the cationic copolymerization of cyclic dienes, the stability of cycloalkenyl cation is important to explain the experimental results. The stability of cation could be discussed in terms of the pK_{BH}^+ value of Eq. (1) proposed for a base–protonated base ($B-BH^+$) equilibria.

$$B + H^+ \longrightarrow BH^+ \qquad H_0 = pK_{BH}^+ + \log C_B/C_{BH}^+ \qquad (1)$$

pK_{BH}^+ values of cations pertinent to the present investigation have not been determined directly but can be calculated from the values of the related cations on the basis of a reasonable assumption,

pK_{BH}^+ of t-butyl cation (isobutene)	-15.5[9)]
pK_{BH}^+ of cyclopentenyl cation (CPD)	-8.7[10)]
pK_{BH}^+ of cumyl cation (α-MS)	-7.4[11)]*

A large differnce in cation stability between isobutene and CPD is reflected in the large solvent effect on the monomer reactivity ratio of isobutene–CPD copolymerization (see Table VI).

On the other hand, there is little difference between pK_{BH}^+ values of cyclopentenyl cation and cumyl cation. And, expectedly, the α-MS–CPD copolymerization was little affected by the solvent polarity.

So far it has been generally accepted that the solvent effect emerges more or less in the copolymerization between monomers of dissimilar structures. However, the present experiment is the first example showing that this is not the case if the stabilities of cations are similar.

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* This is a value reported for 2,4,6-trimethylcumyl cation, but methyl groups on the phenyl group do not seem to affect pK_{BH}^+ value so much.[11] Deno et al. have recommended the use of

$$H_R - \log a_{H_2O} = pK_R'^+ + \log C_{ol}/C_R^+$$

instead of Eq. (1) for mono- or diaryl olefin–protonated olefin equilibria when the olefin is produced by an acid-catalyzed dehydration of alcohol in situ, and reported a $pK_R'^+$ value of cumyl cation to be -12.2.[11] However, Eq. (1) seems to be applicable to describe the equilibria, too.[12] In the present chapter, for the comparison with pK_{BH}^+ values of t-butyl cation and cyclopentenyl cation Eq. (1) was used to calculate pK_{BH}^+ of cumyl cation on the basis of Deno's experimental data.

The intrinsic viscosity of α-MS–CPD copolymer was nearly or higher than unity and not extremely lower than those of homopolymers. This is in marked contrast to isobutene-styrene copolymer,[7] where the intrinsic viscosity of copolymer was low. This may be explained in terms that there is little difference between cation stabilities in the present case, so that the cross-transfer reaction is not important.

The autooxidation of α-MS–CPD copolymer proceeds much slower than that of PCPD, but the oxidation rate is roughly proportional to the content of CPD, it is safe to say that only a CPD unit in the copolymer affects the oxidation. The resistance to the oxidation of PCPD is not improved by copolymerizing α-MS.

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Chapter 6

Copolymerization of Cyclopentadiene with 2-Chloroethyl Vinyl Ether and Some Properties of the Copolymer

INTRODUCTION

Cyclopentadiene (CPD) is very reactive in cationic polymerization as evidenced by the large propagation rate constant[1] and the copolymerization study with α-methylstyrene,[2] while 2-chloroethyl vinyl ether (CEVE) is a representative of vinyl ethers which are known as cationically reactive monomers. CEVE was copolymerized not only with other vinyl ethers but also with various monomers such as styrene derivatives.[3]

Thus CPD and CEVE were supposedly copolymerized and expected to give elastomers. In fact, a Japanese patent[4] covered the copolymerization of isopropyl vinyl ether with CPD and vulcanization of the copolymer, although there has been no academic investigation. We focussed our attention on the solvent effect in cationic copolymerization and the properties of the polymer as elastomer. CPD differs from CEVE in structure but both have high reactivities, so the presence or absence of solvent effects is expected to shed a light on the nature of the solvent effect in cationic polymerizations.

EXPERIMENTAL

Polymerization

All the reagents used were washed and distilled at least three times on appropriate drying agents. CPD was purified as described earlier in this thesis and finally distilled onto polymerization flask under high vacuum. Solvent, CEVE, and catalyst solution were introduced into the flask with a syringe through a self-sealing rubber cap under dry nitrogen atmosphere. The copolymerizations were carried out at the dry ice–methanol temperature. The methanol insoluble polymer was recovered and the composition analyzed by nuclear magnetic resonance (NMR) spectroscopy. Limiting viscosity numbers of the polymers were determined at 30°C in toluene.

Oxidation of copolymer

The copolymer was subjected to oxidation at room temperature in air. The degree of the oxidation with the elapse of time was estimated from two absorption bands in the infrared (IR) spectra at 3400 cm^{-1} and 1710 cm^{-1}, assignable to hydroxyl and carbonyl groups, respectively. Films for the spectroscopic measurements were prepared by casting the benzene solutions of the polymers with or without antioxidant (phenyl-β-naphthyl amine) onto glass plates floated on mercury.

Vulcanization of copolymer

Copolymers were compounded with sulfur and other additives on a roll-mill at room or a little elevated temperature, the

recipe of which is shown in Table I, followed by press-curing at 150°C for 10 or 20 min. Tensile properties and solubility in benzene at room temperature were measured to characterize the vulcanizates.

Dynamic measurements

Dynamic mechanical properties were measured on Viscoelasto Spectrometer (Iwamoto Seisakusho Co.). Dynamic modulus E' and dynamic loss factor E" were measured at 10 c/s from -120°C to room temperature for polycyclopentadiene (PCPD), poly-2-chloroethyl vinyl ether (PCEVE), and vulcanizates of the copolymers.

TABLE I

Compounding Recipe

Material	Parts (weight)
Copolymer	100
Zinc oxide	5
Stearic acid	1
Sulfur	2
Accelerator CZ[a]	1.5
Antioxidant D[b]	2

[a] Cyclohexyl benzothiazyl sulfenamide.

[b] Phenyl-β-naphthyl amine.

RESULTS

In the case of toluene and methylene chloride, polymerization solutions were optically clear. In nitroethane the system was not completely homogeneous. The polymers obtained were soluble in toluene or chloroform, but the polymer produced in methylene chloride at high conversions had a lower solubility than the others.

1. Monomer Reactivity Ratios.

The results of the copolymerization in toluene are shown in Table II and in Figure 1. All polymerizations were stopped at

TABLE II

Copolymerization of CPD and CEVE in Toluene[a]

No.	CEVE ml	CPD ml	CPD[b] mole %	$BF_3 \cdot OEt_2$ mmole/l	Time min	Conv. %	CPD[c] mole %
1	8.0	0	0	20	5	2.9	0
2	6.5	0.45	8.9	30	5	6.4	1.9
3	7.1	0.95	16	35	5	13.6	6.1
4	6.1	1.95	31	35	5	13.2	15.3
5	5.2	2.8	44	35	5	11.1	23.5
6	4.9	3.1	47	30	5	4.6	33.3
7	4.8	3.2	48	30	5	4.4	33.1
8	3.6	4.4	63	35	5	3.7	49.1
9	3.4	4.6	64	30	5	3.1	57.0
10	2.1	5.9	80	30	5	5.1	63.8
11	1.6	6.4	85	30	5	4.2	68.2
12	0	8.0	100	20	5	1.7	100

[a] Catalyst; $BF_3 \cdot OEt_2$. Temperature; -78°C.

[b] CPD fraction in monomer feed.

[c] CPD units in copolymer.

low conversions by choosing the suitable catalyst concentrations and the polymerization time. From these data monomer reactivity ratios were determined according to the Mayo-Lewis equation. Values are shown in Table III evaluated from the method of the Fineman-Ross, the intersection method, and the symmetrically linearized Fineman-Ross equation.[5)]

TABLE III

Monomer Reactivity Ratios Calculated from Different Methods for the Copolymerization of CPD (M_1) with CEVE (M_2) in Toluene[a]

Method	r_1	r_2	$r_1 \cdot r_2$
FINEMAN-ROSS (r_1 = slope)	0.55 ± 0.5	2.1 ± 0.4	1.15
FINEMAN-ROSS (r_2 = slope)	0.62 ± 0.1	2.5 ± 0.6	1.55
Intersection	0.60 ± 0.2	2.8 ± 0.3	1.68
Modified FINEMAN-ROSS[b]	0.73 ± 0.3	3.5 ± 0.6	2.6

[a] Catalyst; $BF_3 \cdot OEt_2$. Polymerization temperature; -78°C.

[b] Symmetrically linearized equation, see ref. 5).

Values by the methods of the Fineman-Ross and the intersection are in good agreement with each other, but a little different from those calculated by the modified Fineman-Ross equation. Theoretical lines by these values are plotted in Figure 1. It is demonstrated that the values calculated by various methods fit the experimental fairly well. All these data indicate CEVE is more reactive than CPD towards either carbonium ion in toluene solution.

Methylene chloride and nitroethane were employed as polar solvents for the copolymerization. The results are shown in Table IV and in Figure 2. From the table it is clear that the monomer reactivity ratios evaluated by different methods are in agreement. The integrated Mayo-Lewis equation was used in

TABLE IV

Monomer Reactivity Ratios for the Copolymerizations of CPD (M_1) with CEVE (M_2) in Polar Solvents[a]

Solvent	Method	r_1	r_2	$r_1 \cdot r_2$
	FINEMAN-ROSS (r_1 = slope)	1.80 ± 0.4	1.10 ± 0.5	1.98
	FINEMAN-ROSS (r_2 = slope)	1.85 ± 0.3	1.05 ± 0.1	1.94
CH_2Cl_2	Intersection	2.2 ± 0.6	1.00 ± 0.5	2.2
	Modified FINEMAN-ROSS	1.87 ± 0.2	1.11 ± 0.2	2.1
$C_2H_5NO_2$	Integrated MAYO-LEWIS	3.0 ± 0.6	1.6 ± 0.6	4.8

[a] Catalyst; $BF_3 \cdot OEt_2$. Polymerization temperature; -78°C.

the case of nitroethane because the conversions were high. These monomer reactivity ratios reveal that CPD is somewhat more reactive in polar solvents than CEVE. Also it can be seen that the increase of solvent polarity makes the product $r_1 \cdot r_2$ larger. This is reflected on the copolymer composition curve in Figure 2 which is slightly S-shaped, and in nitroethane, which has the highest dielectric constant of the three solvents studied, both r_1 and r_2 exceeds unity. These facts seem to indicate a tendency to form block copolymers in polar solvents.

The plot of $\log(M_1/M_2)$ vs. $\log(dM_1/dM_2)$ is shown in Figure 3.

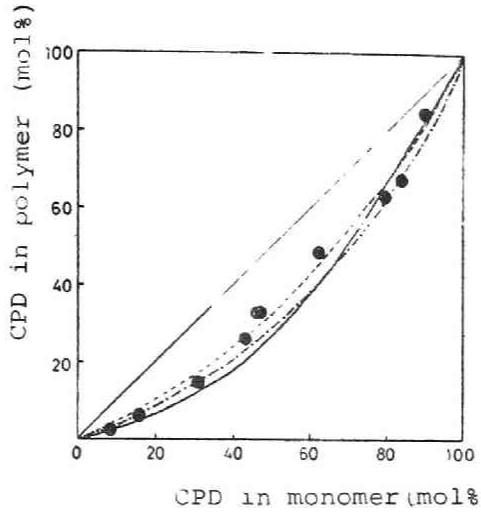

Fig. 1. Copolymer composition curve of CPD (M_1) and CEVE (M_2). Catalyst $BF_3 \cdot OEt_2$, Solvent toluene, Temp. -78°C. ——— Modified Fineman-Ross (r_1 = 0.73, r_2 = 3.5), ------ Fineman-Ross (r_1 = 0.55, r_2 = 2.1), —·—·— Intersection (r_1 = 0.60, r_2 = 2.8).

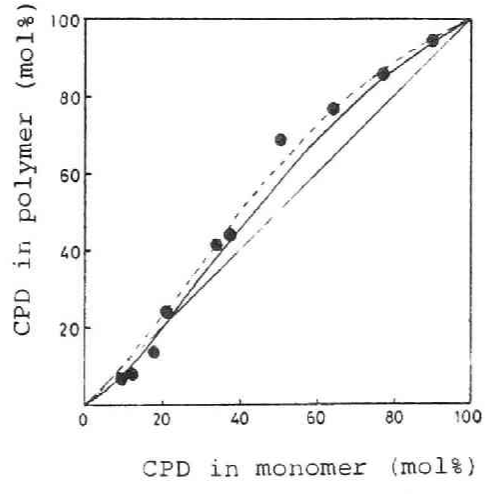

Fig. 2. Copolymer composition curve of CPD (M_1) and CEVE (M_2). Catalyst $BF_3 \cdot OEt_2$, Solvent methylene chloride, Temp. -78°C. ——— Modified Fineman-Ross (r_1 = 1.87, r_2 = 1.11), —·—·— Intersection (r_1 = 2.2, r_2 = 1.0).

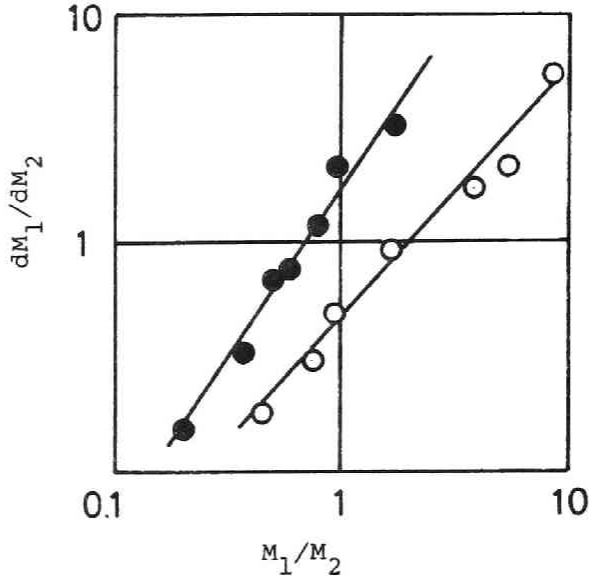

Fig. 3. Relationship between $\log(M_1/M_2)$ and $\log(dM_1/dM_2)$ in the copolymerization of CPD (M_1) and CEVE (M_2). (○) in toluene. (●) in methylene chloride.

Linearity was established either in toluene or in methylene chloride, i.e., the following equation proposed by O'Driscoll[6] holds in both solvents:

$$\frac{dM_1}{dM_2} = K\left(\frac{M_1}{M_2}\right)^a$$

K values are 0.48 in toluene and 1.7 in methylene chloride, and a values are 1.06 and 1.5 respectively. The values K and a conform well with r_1 and r_2, showing the validity of Mayo-Lewis equation for these copolymerization systems.

2. Viscosity and Oxidation of Copolymers.

Limiting viscosity numbers of copolymers are shown in Table V. With $BF_3 \cdot OEt_2$ catalyst, PCPD has higher viscosity than PCEVE, and

TABLE V

Limiting Viscosity Numbers of the Copolymers

Solvent[a]	Polymer	Conversion %	CPD units mole %	$[\eta]^b$ dl/g
	PCPD			0.99
Toluene	PCEVE			0.28
	Copolymer	83.4	51	0.78
	Copolymer	21.6	52	0.34
CH_2Cl_2	Copolymer	16.0	67	0.50
$C_2H_5NO_2$	Copolymer	57.2	26	0.34

[a] Polymerization solvent.

[b] In toluene solution, at 30°C.

the copolymer with higher content of CPD unit tends to have higher viscosity. It seemed not being so difficult to obtain the copolymer with [η] near or more than unity by choosing the suitable polymerization conditions.

PCPD is known to be oxidized quickly in air and soon becomes insoluble. The CPD-CEVE copolymer was highly susceptible to air oxidation too, as is illustrated in Figure 4. Figure 4 shows that IR spectra of the copolymer film containing about 1 % of phenyl-β-naphthyl amine remained practically unchanged over 70 days. Not only the phenolic antioxidant[2)] but the amine compound is proved to be strongly effective.

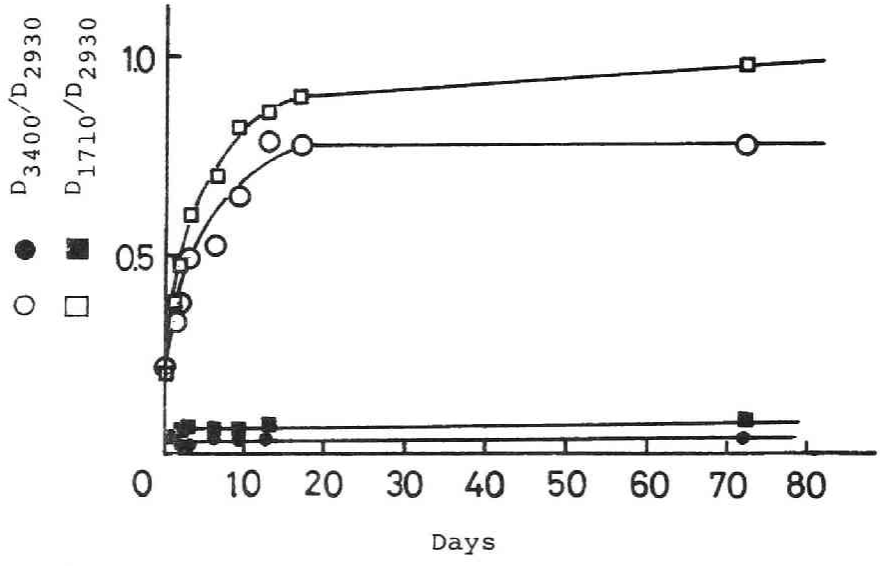

Fig. 4. Change of IR spectrum of CPD–CEVE copolymer on oxidation. (●)(■) Film containing antioxidant, (○)(□) Film not containing antioxidant. Copolymer polymerized in toluene, CPD 51 mole%.

3. Vulcanization and Dynamic Properties.

PCPD was too hard to compound on a roll-mill at room temperature, but the copolymers were soft enough at room temperature or in some cases at 50°C. The copolymer (polymerized in toluene, CPD 51 mole %, $[\eta]$ = 0.78) was compounded with ingredients according to the recipe shown in Table I and vulcanized at 150°C under heat press. Figure 5 shows the stress-strain curves of the vulcanizates. The gum vulcanizates exhibited high tensile strength exceeding 100 kg/cm^2 at break and ten minutes were sufficient for curing. The cured copolymers did not show any solubility in benzene at room temperature, whereas the cured samples of the blend of the copolymer and PCEVE, and that of PCPD and

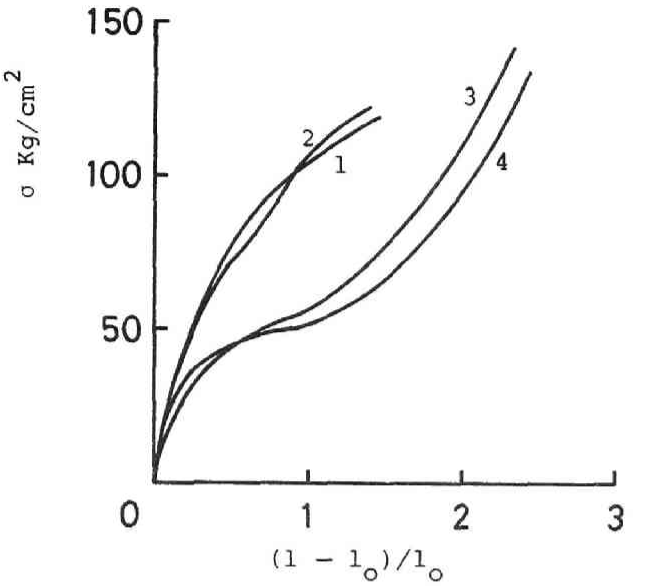

Fig. 5. Stress-strain curves of the copolymer vulcanizates. Copolymer polymerized in toluene, CPD 51 mole%. Conditions for vulcanization: 1. Temp. 150°C, Time 20 min, Carbon black stock. 2. Temp. 150°C, Time 10 min, Carbon black stock. 3. Temp. 150°C, Time 20 min, Gum stock. 4. Temp. 150°C, Time 10 min, Gum stock.

PCEVE* both were soluble in benzene as shown in Table VI. The IR spectra of the dissolved parts of the samples showed that only PCEVE was soluble. Accordingly the weight loss in Table VI was exclusively due to dissolved PCEVE. Percents of the dissolved PCEVE are indicated in the third column.

Dynamic moduli and loss factors of PCPD, PCEVE, and the cured samples of the copolymer are plotted in Figure 6 as a function of

---

* The benzene solutions of PCPD and PCEVE were mixed and benzene was evaporated. The resultant film was compounded on roll-mill at a little elevated temperature and cured.

TABLE VI

Solubility Behaviour of the Cured Samples of the Copolymer and the Polymer Blends[a]

Sample	Weight loss[b] %	PCEVE loss[c] %
Copolymer (CEVE mole % = 26)	0	0
Copolymer (CEVE mole % = 49)	0	0
Blend[d] (CEVE mole % = 48)	57.0	95
Blend[e]	7.0	21

[a] Solvent benzene, at room temperature.

[b] Weight percents of polymer soluble in benzene.

[c] Weight loss was exclusively due to PCEVE, so percents of dissolved PCEVE for the original PCEVE in samples were shown.

[d] Blend of PCPD and PCEVE.

[e] Blend of the copolymer (CPD mole % = 50, 2 g) and PCEVE (1 g).

temperature. PCEVE has glass transition at -5°C, while PCPD and the vulcanizate of the copolymer at +10°C.

DISCUSSION

1. Solvent Effect in Copolymerization.

The results described in the present chapter demonstrate an interesting solvent effect on the cationic copolymerization. In a nonpolar solvent CEVE is more reactive than CPD towards either carbonium ion and $r_1 \cdot r_2$ is nearly unity, whereas in a polar

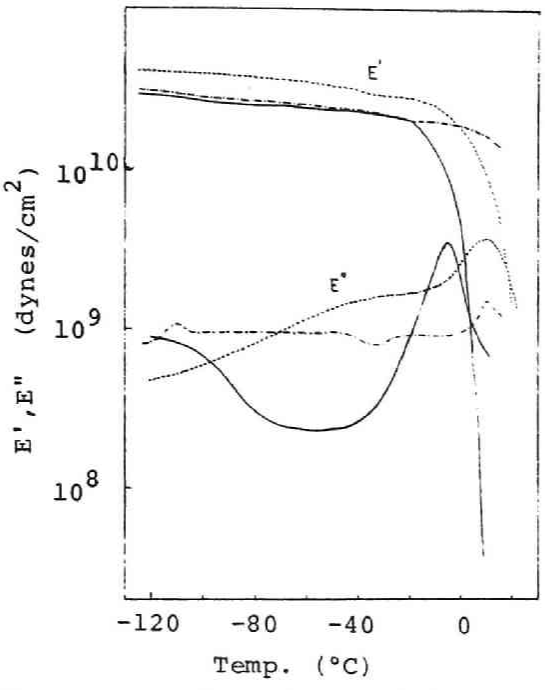

Fig. 6. Temperature dependence of dynamic moduli (E') and loss factors (E") of PCPD, PCEVE, and CPD-CEVE copolymer. measured at 10 c/s. (———) PCEVE, (-----) PCPD, (·—·—·—·) Vulcanizate of the copolymer (polymerized in toluene, CPD 51 mole %).

solvent the order of the reactivity reverses and $r_1 \cdot r_2$ is larger than unity. These results are very similar to those of the copolymerization of isobutene with styrene,[8,9] and a few explanations have been proposed. For example, Imanishi et al.[8] explained the phenomena in terms of the monomer nucleophilicity and the stability of carbonium ion. According to their account, isobutene is more nucleophilic than styrene and the carbonium ion derived from styrene is more stable than that from isobutene.

The same explanation is possible for the present system, i.e., the alkoxy carbonium ion seems to be more stable than cycloalkenyl one and CPD to be more nucleophilic than CEVE. In polar solvents

the ions are highly solvated and the difference of their stabilities is lessened. Therefore the copolymerization reactivity is mainly governed by the nucleophilicity of the monomer. On the other hand the growing ions have to be stabilized in some way in nonpolar solvent, and the stability of the carbonium ion is an important factor. "Preferential solvation" proposed by Overberger et al.[9] could also be possible, but the behaviour of CPD in polar solvents can only be interpreted by the intrinsic reactivity of the monomer without solvation, which may be equivalent to nucleophilicity. Thus, two parameters must be taken into consideration, and the "preferential solvation" as a sole interpretation could not be adopted.

There has been no direct observation comparing the stabilities of alkoxy cation and cycloalkenyl cation, but both have greater stabilities than other carbonium ions.[10,11] Under the present conditions alkoxy cation is likely to be more stable. In addition, CPD is more nucleophilic than CEVE according to the above explanation, which may reflect on the large propagation rate constant of CPD[1] in cationic polymerization. Considering the present result and earlier copolymerization studies.[2,12] the order of the stability of the carbonium ion is,

$$(\text{CEVE})^+ > (\text{CPD})^+ \simeq (\alpha\text{-Methylstyrene})^+ > (\text{Isobutene})^+.$$

This seems to be a reasonable order.

We can use several methods to calculate the monomer reactivity ratio. The three of them are compared in Tables III and IV, i.e., the Fineman-Ross, the intersection, and the modified Fineman-Ross.

The first and the second are employed by a number of polymer chemists for convenience but a few shortcomings were pointed out by several authors. The use of improved equations[5] or method[13] has been recommended. So far as our data on the cationic copolymerization of CPD with CEVE are concerned, modified equation proposed by Erzielev et al.[5] gave the same values as other methods within experimental errors. Therefore advantages of the modified equation were not established here. Coincidence among different methods assures the correctness of the obtained values, despite the pointed weakness of each method used.

2. Physical Properties of Copolymer.

The copolymer was highly susceptible to air oxidation as demonstrated. The resistance to oxidation was not improved by copolymerizing CEVE but addition of phenyl-β-naphthyl amine was strongly effective. It is reported that the copolymer of CPD with o-vinyl phenol showed resistance to oxidation.[14] From this point of view, comonomers having amino groups are expected to be suitable comonomers for antioxidation, too.

The copolymer was able to be compounded on a roll-mill at room temperature, but PCPD was not so. Cured samples were insoluble in benzene and evidenced to be crosslinked. The results in Table VI indicate that true copolymers were formed, taking the large difference between the cured samples of the homopolymer mixture and the copolymers into account.

Usually, the glass transition temperature (Tg) of random copolymer lies between Tg's of the two homopolymers.[7] Therefore

glass transition of the random copolymers was expected to be between -5°C and +10°C, but the present data did not demonstrate this clear. The correspondence of the kinetic data ($r_1 \cdot r_2 \simeq 1$) and the dynamic data (Tg) is not fully established, probably because of the crosslinking.

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Chapter 7

Copolymerization between Cyclic Dienes and Their Relative Reactivities

INTRODUCTION

Relative reactivities of cyclic dienes were discussed in Chapter 4 on the basis of the results of their homopolymerizations. However, the reactivity of monomer can not be fully elucidated only from the homopolymerization data. In this connection the copolymerizations between cyclic dienes were carried out to compare their inherent reactivities in propagation reaction. The reactivity of cyclic dienes relative to cyclopentadiene as the standard was discussed in comparison with other monomers, i.e., styrene derivatives, vinyl ethers, and alkenes, which have been copolymerized with cyclic dienes.

EXPERIMENTAL

Materials

Monomers 1,3-Cyclohexadiene (CHXD) was synthesized and purified as reported.[1] Methylcyclopentadiene (MCPD), cyclopentadiene(CPD), 1,3-cycloheptadiene (CHPD) and 1,3-cyclooctadiene (COD) were obtained as described in earlier chapters.

Other reagents employed were purified as described in earlier

chapters.

Procedures

Copolymerizations of MCPD and CPD were carried out as described in Chapter 2. Copolymer compositions were analyzed by infrared spectroscopy. Copolymerizations among CHXD, CHPD and COD were conducted under dry nitrogen atmosphere and the residual monomer concentration was determined by gas chromatography at determined time intervals (column dinonyl phthalate, column temperature 90°C).

RESULTS

1. Copolymerization of Methylcyclopentadiene with Cyclopentadiene.

For the copolymerization of MCPD with CPD, the copolymer composition was analyzed by infrared spectroscopy, the absorption at 830 cm^{-1} being used as a key band. This absorption was ascribed to C–H out-of-plane deformation of trisubstituted ethylene[2] which exists only in polymethylcyclopentadiene (PMCPD). The mixtures of PMCPD and polycyclopentadiene (PCPD) with the known compositions were prepared and subjected to infrared spectroscopy. Figure 1 shows the calibration curve between the copolymer composition and the infrared spectrum, which was used to analyze the copolymer composition throughout this work. The copolymer composition determined by this method is in good agreement with that determined by nuclear magnetic resonance measurement of the copolymer.

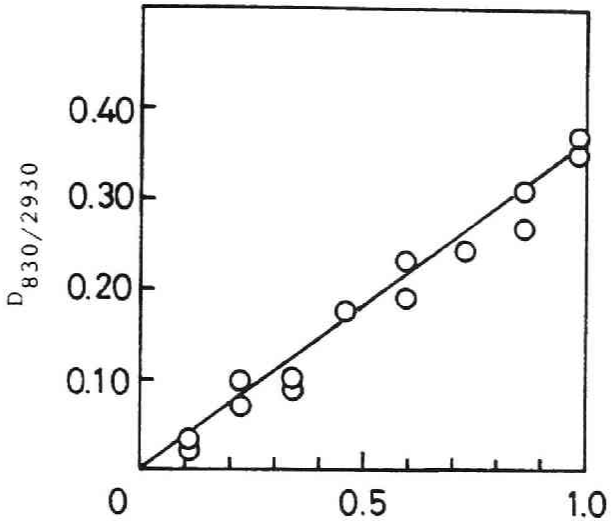

Fig. 1. Calibration curve for the determination of copolymer composition of MCPD and CPD.

The compositions of copolymer obtained by $TiCl_4$-trichloroacetic acid (TCA) in toluene are plotted against the monomer feed in Figure 2. It was found that MCPD is more reactive in the propagation reaction than CPD. The intrinsic viscosities of the copolymers lay in the range of 0.3 – 0.5.

The effect of solvent polarity on the monomer reactivity ratio was investigated with the copolymerization catalyzed by $SnCl_4$-TCA. As is seen in Figure 3, no serious effect of the solvent dielectric constant was observed. Since in all copolymerizations the conversions was kept below 10 %, the Mayo-Lewis differential equation was used to calculate the monomer reactivity ratios (M_1 MCPD, M_2 CPD):

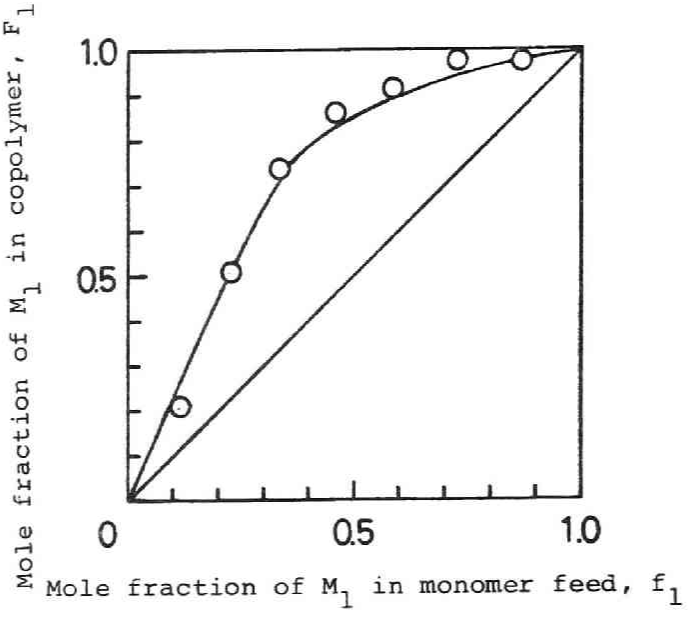

Fig. 2. Copolymer composition curve of MCPD (M_1) and CPD (M_2) catalyzed by $TiCl_4$-TCA at -78°C. Total monomer concentration 15 vol % (1.8-2.0 mole/l). $[C]_o$ ca. 1.0 mmole/l. Solvent toluene.

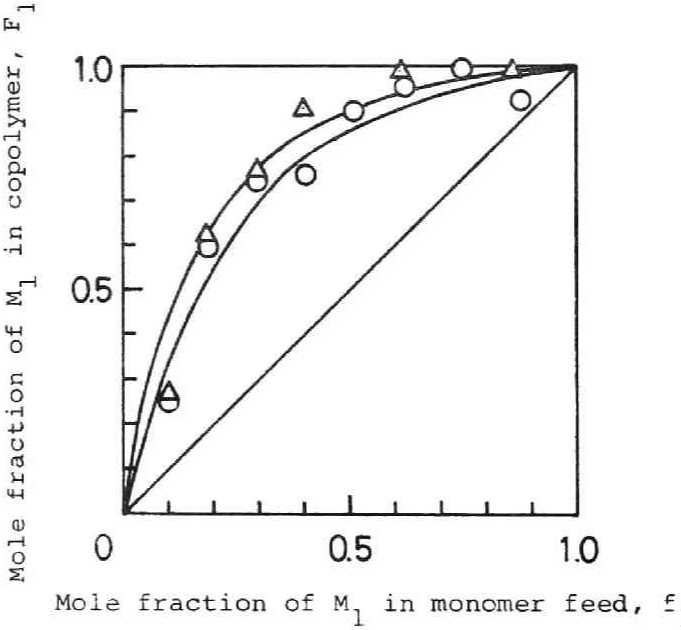

Fig. 3. Copolymer composition curves of MCPD (M_1) and CPD (M_2) catalyzed by $SnCl_4$-TCA at -78°C. ○ in toluene, $[C]_o$ ca. 0.6 mmole/l. △ in methylene chloride, $[C]_o$ ca. 0.4 mmole/l. Total monomer concentration 20 vol % (2.4-2.7 mole/l).

$r_1 = 8.5 \pm 3.5$ $r_2 = 0.36 \pm 0.26$ in toluene,

$r_1 = 14.9 \pm 5.6$ $r_2 = 0.42 \pm 0.23$ in methylene chloride.

Comparison of Figure 2 with Figure 3 showed that the catalyst had little effect on the monomer reactivity ratio.

2. Copolymerization between Conjugated Cyclic Dienes.

Possible pairs of three conjugated cyclic dienes, CHXD, CHPD, and COD, were copolymerized in methylene chloride at 0°C. The catalyst solution was added to the monomer mixture in methylene chloride and the consumption of each monomer was followed by gas chromatography. The relative reactivity of monomer was estimated from the initial rate of monomer consumption. The results are shown in Figures 4-6. In Figure 7, the monomer consumption for the copolymerization of CHXD and COD at -78°C is shown. Initial rates of monomer consumption were determined and are collected in Table I. These results clearly demonstrate the relative reactivity of the cyclic dienes falls in the order:

CHXD > CHPD > COD

Comparison of the homopolymerizations of CPD with CHXD,[1] and the copolymerizations of isobutene with CPD and with CHXD[3] show that CPD is much more reactive than CHXD. Thus the reactivities of the five cyclic dienes studied decrease in the order:

MCPD > CPD > CHXD > CHPD > COD

Apparently, the increse of the ring size decreases the reactivity of conjugated cyclic dienes.

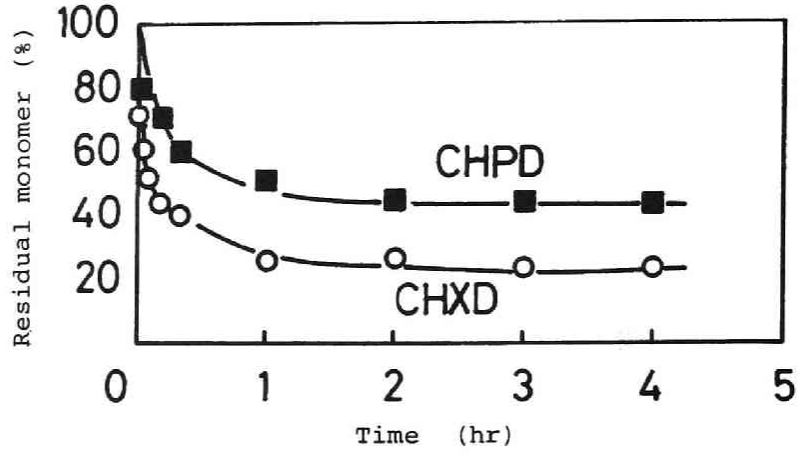

Fig. 4. Copolymerization of CHXD and CHPD by $SnCl_4$-TCA in CH_2Cl_2 at 0°C (Time dependence of residual monomer concentrations relative to initial monomer concentration). $[C]_o$ 10 mmole/l.

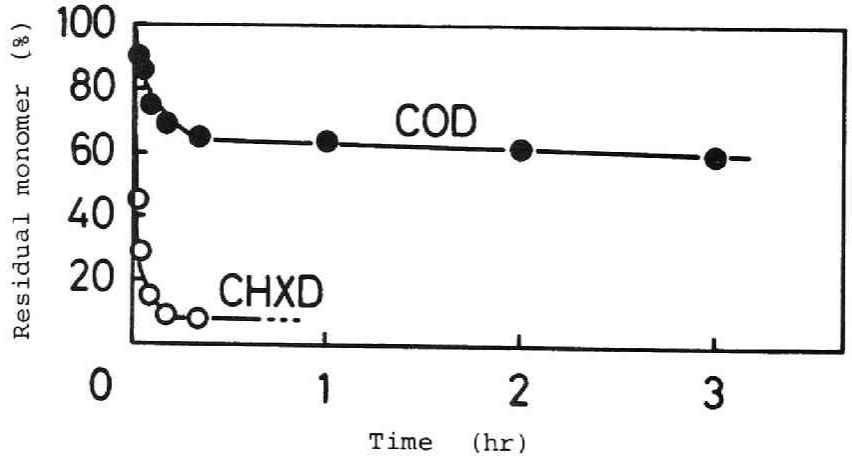

Fig. 5. Copolymerization of CHXD and COD by $SnCl_4$-TCA in CH_2Cl_2 at 0°C. $[C]_o$ 20 mmole/l.

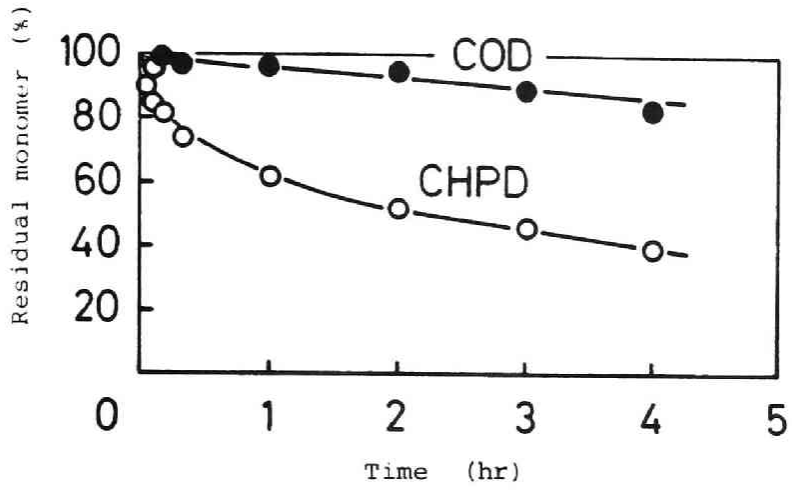

Fig. 6. Copolymerization of CHPD and COD by $SnCl_4$-TCA in CH_2Cl_2 at 0°C. $[C]_o$ 30 mmole/l.

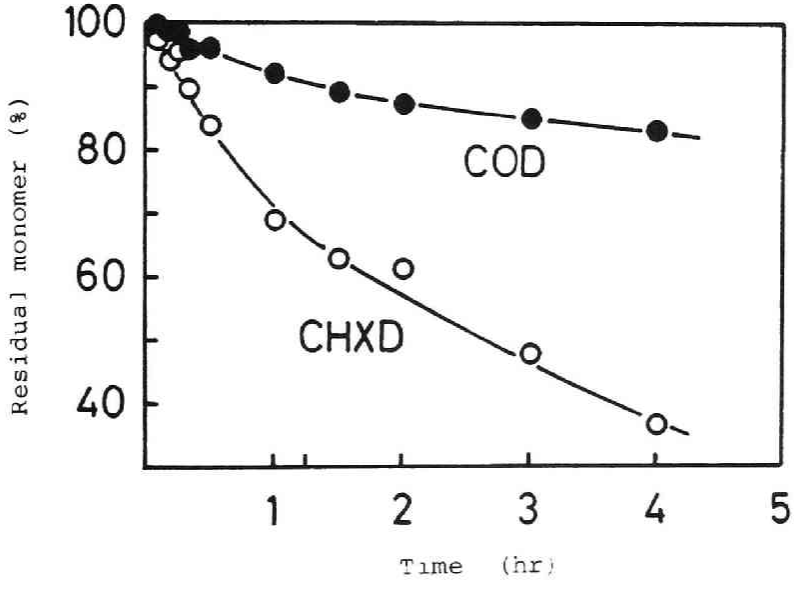

Fig. 7. Copolymerization of CHXD and COD by $SnCl_4$-TCA in CH_2Cl_2 at -78°C. $[C]_o$ 40 mmole/l.

TABLE I

Initial Rate of Monomer Consumption in the Copolymerizations of CHXD, CHPD, and COD

Monomer Pair	$[C]_o$ (mmole/l)	$R_{p_o}/[M]_o$ (sec^{-1})
CHXD	10	2.8×10^{-2}
CHPD		2.2×10^{-2}
CHXD	20	5.5×10^{-2}
COD		1.36×10^{-2}
CHPD	30	4.0×10^{-3}
COD		0.52×10^{-3}

Solvent CH_2Cl_2, temperature 0°C, catalyst $SnCl_4$-trichloroacetic acid.

DISCUSSION

1. Relative Reactivity of Conjugated Cyclic Dienes.

Investigation of the homopolymerization of MCPD demonstrated that MCPD was more reactive than CPD.[4] However, polymerizations catalyzed by $TiCl_4$-TCA seemed to be an exception, where more catalyst was needed than in the polymerization of CPD to get the same conversion.[4] The possible reason for this anomaly is the more important catalyst-consuming reaction with MCPD than with

CPD. The copolymerization of MCPD with CPD showed that MCPD is about ten times as reactive as CPD. This indicates unambiguously the larger reactivity of MCPD than CPD in the propagation reaction, and at the same time the peculiarity of $TiCl_4$-TCA as a catalyst. The higher reactivity of MCPD than CPD is accounted for in terms of an effect of a methyl group. In fact, with 1-methylcyclopentadiene the pKa value of its conjugated cation has been calculated to be -5.3,[5,6] and with CPD it is -8.7.[5,6] These values mean that the MCPD cation is more stabilized by the action of a methyl group than the CPD cation, and that the nucleophilicity of MCPD is also enhanced by a methyl substitution. These electronic effects of the methyl group facilitate the cationic polymerization of MCPD and the catalyst-consuming side reactions with $TiCl_4$ as well.

Effect of ring size on the reactivity was rather simple, i.e., the reactivity decreases with the increase of ring size monotonously. Undoubtedly the steric structure of the monomers is very important to determine the reactivity and this must affect the electronic state in the monomers. There have been published several reports on the conformation of cyclic dienes.[7-11] The detailed structure of each diene is still under consideration (for example, see ref. 11), but the general features of these compounds have been established.[7,8] In particular, the dihedral angle i.e. the angle between the two planes on which each of the two double bonds lies must have some bearing on the electronic state of the conjugated cyclic dienes.[8] The dihedral angles reported for the conjugated cyclic dienes relevant to the present

investigation are set out in Table II together with the abosrption maxima.[8] The increase in ring size induces the increase of the dihedral angles leading to less conjugation between the two double bonds, as evidenced by the hypsochromic shift of the absorption maxima ($\pi \longrightarrow \pi^*$ transition, CPD being an exception[12]).

TABLE II

The Dihedral Angles and the Electronic Spectra of Conjugated Cyclic Dienes[8]

Compound	θ (deg.)	λ cal.[a] (nm)	λ expl. (nm)
CPD	0	250	242
CHXD	17	245	256.5
CHPD	52	230	248
COD	64	216	229

[a] Based on the method of Pariser and Parr [J. Chem. Phys., 21, 466, 767 (1953)].

The reactivity of conjugated cyclic dienes apparently seems to be governed by the degree of conjugation between the two double bonds, that is, the higher the degree of conjugation, the more reactive the cyclic diene. We can only say at present that the conjugation stabilizes the transition state more than the initial state. In this regard, cyclohexene, for example, which may be regarded as an extreme of loosing conjugation in 1,3-cyclohexadiene, show little tendency to polymerize by cationic

initiators.[13]

2. Reactivity of Cyclopentadiene Relative to Vinyl Monomers and a General Explanation of the Monomer Reactivity in Cationic Polymerization.

As a standard of conjugated cyclic dienes, the copolymerization data of CPD with vinyl monomers are collected in Table III. In the table, the effect of solvent polarity on the monomer reactivity ratios is very interesting. Some explanations have been proposed for the solvent effect in cationic copolymerization,[16,17] and the explanation in terms of the nucleophilicity of monomer and the stability of carbonium ion intermediate proposed by Imanishi et al.[17] seems to be the most suitable to account for the copolymerization behaviours of cyclic dienes as shown in Chapters 5 and 6. For example, the absence of solvent effect in the copolymerization of CPD with α-MS[15] was interpreted in terms that the propagating carbonium ion derived from CPD is as stable as that from α-MS, and the higher reactivity of CPD in the same copolymerization in terms of the higher nucleophilicity of CPD than α-MS. For CEVE–CPD pair,[14] $(CEVE)^+$ would be more stable than $(CPD)^+$ and CPD more nucleophilic than CEVE. In actuality, CEVE was more reactive than CPD in toluene. This could be because in nonpolar solvents the stability of propagating species is more important than the nucleophilicity of monomer to determine the monomer reactivity. Carbonium ions are stabilized by solvation in polar solvents, so the nucleophilicity of monomer is increasingly important to determine the

TABLE III

Monomer Reactivity Ratios of CPD (M_2)

M_1	r_1	r_2	Solvent	Catalyst	Temp. (°C)	Ref.
CEVE[a]	2.8	0.60	toluene	$BF_3 \cdot OEt_2$	-78	14
"	1.00	2.2	CH_2Cl_2	"	"	"
α-MS[b]	0.47	1.23	n-hexane	"	"	15
"	0.66	1.62	toluene	"	"	"
"	0.67	1.52	CH_2Cl_2	"	"	"
IB[c]	0.60	4.5	toluene	"	"	3
"	0.73	1.86	CH_2Cl_2	"	"	"

[a] 2-Chloroethyl Vinyl Ether

[b] α-Methylstyrene

[c] Isobutene

monomer reactivity as the solvent polarity increases. Therefore, in polar solvents more nucleophilic CPD should be a little more reactive than CEVE, which was the case. The analogous explanation has been presented for IB–CPD.[3)]

There have been published differnt types of the solvent effect on the cationic copolymerizations, i.e., a small solvent effect in the copolymerization of styrene (St) with p-chlorostyrene (p-ClSt),[18)] a large solvent effect in the copolymerization of St with IB,[16,17)] and an intermediate solvent effect in the copolymerization of α-MS with CEVE.[19)] If the above-mentioned explanation

holds for these copolymerization systems, the monomer nucleophilicity and the carbonium ion stability should be in the following order:

The nucleophilicity of monomer

CPD > CEVE > α-MS > IB > St > p-ClSt

the stability of carbonium ion

$(CEVE)^+ > (CPD)^+ \simeq (\alpha\text{-MS})^+ \simeq (St)^+ \simeq (p\text{-ClSt})^+ > (IB)^+$

It should be noted here that sometimes we assess the same aspect in differnt terms, nucleophilicity of olefin or stability of ion. However in the above, the nucleophilicity or stability was separately considered as the influencing factor on reactivity. The order of the stability of carbonium ions is consistent with the recent investigations on carbonium ions.[20] According to the above considerations, cycloalkenyl cation is almost as stable as aryl cations. It is interesting that CPD is very nucleophilic and cyclopentenyl cation is very stable, though CPD has no electron-donating substituent such as alkoxy group. The order of the nucleophilicity of vinyl monomers proposed above should be scrutinized by more experimental work.

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PART III

PROPAGATION RATE CONSTANTS IN THE CATIONIC POLYMERIZATION OF CYCLOPENTADIENE

Chapter 8

Polymerization with Titanium Tetrachloride-Trichloroacetic Acid Catalyst

INTRODUCTION

For the mechanistic clarification of chemical reactions kinetics is a very useful method; this applies also to the polymerization reactions. In free-radical polymerization not only the overall kinetics but also the rate constants of elementary reactions have been studied in detail, and the mechanisms of elementary reactions have been discussed further. In the case of anionic polymerization, kinetic studies of living polymer systems have made much contribution to an elucidation of the polymerization mechanism. On the other hand, such general kinetic patterns have not been established in cationic polymerization, one reason clearly being the paucity of data about rate constants of elementary reactions. However much attention has recently been focused on the measurement of rate constants and some useful conclusions have been obtained.[1] Cationic polymerization with iodine by Kanoh et al.[2] and the polymerizations of styrene with sulfuric acid[3,4] and with perchloric acid[5] by Pepper et al. are typical examples. In some cases, however, the detailed study presented rather complicated problems.[6] However

in the case of cationic polymerization catalyzed by Friedel–Crafts halide only a few rate constants have been reported.[7-10]

The cationic polymerization and copolymerization of cyclic dienes have been described in Parts I and II. From these studies, cyclic dienes were found to be very reactive in cationic polymerization and to show complicated but interesting kinetic features. In the system cyclopentadiene (CPD)–titanium tetrachloride-trichloroacetic acid (TCA)–toluene, a very large rate of polymerization and, in particular, non-stationary state kinetics were observed. There was some indication that with a suitable treatment the propagation rate constant might be determined.[11]

With this background, the present investigation was started to establish a general method for obtaining kinetically the propagation rate constant under widely different conditions. To determine the propagation rate constant, the polymerization rate was followed accurately under rigorous conditions by a vacuum technique, and kinetic studies were made.

KINETIC TREATMENT

In Section 1.1 of Chapter 1, the kinetic features in the polymerization of CPD with $TiCl_4$-TCA in toluene using a common technique (not high-vacuum technique) were explained by non-stationary state kinetics similar to that reported by Pepper et al.[3,4] for the polymerization of styrene by protonic acids. In a vacuum system similar elementary reactions may be assumed, that is,

$$C + M \longrightarrow M^* \ (=P_1^*) \qquad k_1 \qquad (1)$$

$$C + 2M \longrightarrow C' \text{ (inactive)} \qquad k_1' \qquad (1')$$

$$P_n^* + M \longrightarrow P_{n+1}^* \qquad k_2 \qquad (2)$$

$$P_x^* \longrightarrow P_x + C \qquad k_3 \qquad (3)$$

$$P_x^* + M \longrightarrow P_x + M^* \qquad k_4 \qquad (4)$$

$$P_x^* \longrightarrow P_x \qquad k_5 \qquad (5)$$

Here eq. (1) is an initiation reaction, eq. (1') represents a kind of catalyst-consuming reaction in which biscyclopentadienyl titanium dichloride is formed from $TiCl_4$ and CPD.[11] Eq. (2) represents a propagation reaction, eqs. (3) and (4) are spontaneous and monomer transfer reactions, respectively; eq. (5) is unimolecular termination. Since CPD is very nucleophilic and $TiCl_4$ electrophilic,[12] they react very rapidly so that the initiation reaction is very fast; that is, $k_1, k_1' \gg k_2, k_3, k_4, k_5$ is reasonably assumed.[2-5,11] Reactions (1) and (1') are competing and one obtains

$$[P^*]_o = \frac{k_1}{k_1 + k_1'[M]_o} [C]_o \qquad (6)$$

where $[C]_o$, $[P^*]_o$, and $[M]_o$ represent the initial concentrations of catalyst, active species, and monomer, respectively. From eqs. (5) and (6)

$$[P^*]_t = [P^*]_o e^{-k_5 t} = \frac{k_1}{k_1 + k_1'[M]_o} [C]_o e^{-k_5 t} \qquad (7)$$

where $[P^*]_t$ represents the concentration of active species at time t. Therefore

$$-\frac{d[M]}{dt} = k_2[P^*]_t[M]_t = \frac{k_1k_2}{k_1 + k_1'[M]_o}[C]_o[M]_t e^{-k_5 t} \qquad (8)$$

For the initial rate of polymerization, we have

$$R_{po} = (-d[M]/dt)_{t=0} = \frac{k_1k_2}{k_1 + k_1'[M]_o}[C]_o[M]_o \qquad (9)$$

$$[M]_o/R_{po} = (1/k_2[C]_o) + (k_1'/k_1k_2[C]_o)[M]_o \qquad (10)$$

According to this equation the values k_2 and k_1'/k_1 can be obtained if R_{po} is measured at various $[C]_o$ and $[M]_o$.

For an alternative method to determine k_2 the integration of eq. (8) yields

$$\ln\frac{[M]_o}{[M]_t} = \frac{k_2}{k_5}\frac{k_1}{k_1 + k_1'[M]_o}[C]_o(1 - e^{-k_5 t})$$

$$= \ln([M]_o/[M]_\infty)(1 - e^{-k_5 t}) \qquad (11)$$

Here $[M]_\infty$ is a monomer concentration at an infinite time, when the final conversion Y is attained. Eq. (11) describes the time course of polymerization and gives the termination rate constant (k_5) by the curve-fitting method.

The final conversion Y can be expressed as

$$Y = 1 - [M]_\infty/[M]_o$$

$$= 1 - \exp\left\{-\frac{k_2}{k_5}\frac{k_1}{k_1 + k_1'[M]_o}[C]_o\right\} \qquad (12)$$

This equation is transformed to

$$\ln(1 - Y) = -\frac{k_2}{k_5}\frac{k_1}{k_1 + k_1'[M]_o}[C]_o \tag{13}$$

$$\frac{1}{\ln(1 - Y)} = -\frac{k_5}{k_2[C]_o} - \frac{k_5 k_1'[M]_o}{k_2 k_1 [C]_o} \tag{14}$$

From this equation, rate constant ratios k_5/k_2 and k_1'/k_1 can be calculated.

Reactions (3) and (4) were not taken into account above, because k_3 and k_4 are considered to be sufficiently smaller than k_2 when a polymer is produced. Moreover, even if k_3 and k_4 are taken into account, the discussion is not altered on a qualitative level. At present these values cannot be evaluated quantitatively.

Based on these kinetic treatments the following studies were made.

EXPERIMENTAL

Apparatus

As widely known, ionic polymerization is influenced strongly by a trace of water or other impurities. So, a handling under vacuum conditions is needed for quantitative study. In addition, the polymerization rate of cyclopentadiene is very large.[11] Therefore we chose an adiabatic condition and followed mechanically the temperature rise accompanying the polymerization.

An outline of the apparatus is shown in Figure 1. These apparatus are principally the same as those developed by Plesch

et al.[13] with some modifications. A denotes the solvent purification lines. The vacuum lines for catalyst are not shown in the figure but the catalyst phials were prepared also under vacuum.

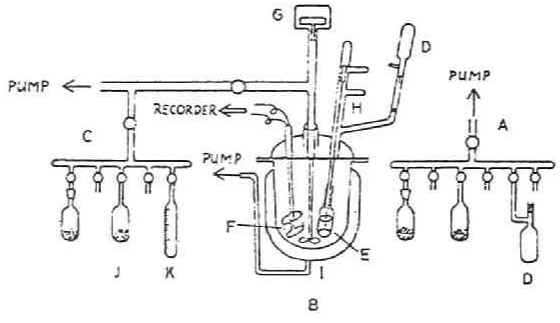

Fig. 1. Apparatus for polymerization.

The equipment for recording the polymerization rate is as follows: platinum wire resistance, Wheatstone bridge, direct current amplifier, oscillograph (photocorder). The platinum wire is submerged in the polymerization solution. The change of resistance accompanying the temperature rise of the reaction solution is amplified and put into the direct-writing oscillograph (Photocorder 2901, Yokogawa Electric Works). The polymerization rate was so large (half life = ca. 5–10sec) that the platinum-resistance thermometer enclosed in a thin glass sheath, which is commercially available, was not sufficient to follow the fast reaction. This sort of thermometer always involves a time lag which cannot be ignored. Also the oscillograph must be used as a recorder instead of the self-balancing Wheatstone bridge to

avoid a time lag.

Reagents

Toluene Toluene was used as a solvent throughout this experiment. Toluene was purified as described previously.[11] It was further purified on a vacuum line using calcium hydride as a drying reagent and finally distilled into a solvent ampoule D fitted with a break-seal.

Cyclopentadiene (CPD) CPD was obtained as described previously.[11] It was collected in a flask connected to line C containing calcium hydride. After the similar treatment as toluene, it was distilled onto baked barium oxide (ampoule J) and stored at low temperatures.

Catalyst Catalyst ampoules were prepared as Plesch did for perchloric acid.[14] Titanium tetrachloride ($TiCl_4$) was distilled twice under reduced pressure and sealed into ampoules fitted with a break-seal. The dilution of catalyst solution was performed on vacuum line and the dilute solution was divided into small glass phials (ca. 2 ml). Trichloroacetic acid (TCA) was pumped for about 10 hr, sublimed, and dissolved in toluene. The solution was distributed in phials. Choosing phials so that the molar ratio of $TiCl_4$ and TCA is nearly unity, the $TiCl_4$ solution were prepared and stored in phials in a similar manner as described above. One of the $TiCl_4$ phials was crushed in cold water and the quantity of $TiCl_4$ was determined by volumetric analysis.[15] TCA was analyzed similarly, and for $TiCl_4$-TCA only the $TiCl_4$ content was determined.

Polymerizations

The toluene ampoule D was connected to the reaction vessel as shown in Figure 1 and a catalyst phial was placed on the holder E. After evacuating the reaction vessel for about 6 hr, the break-seal of D was broken and toluene was introduced into the reaction vessel. The required amount of CPD was distilled into the graduated ampoule K from ampoule J and further distilled into the reaction vessel. On cooling the reaction vessel with liquid nitrogen to ca. -75°C, the jacket of reaction vessel I was evacuated and adiabatic conditions established. The polymerization was started by crushing the catalyst ampoule by handling the breaking device H by a magnet under vigorous stirring. When the influence of stirring was investigated, a synchronous motor and an appropriate gear head were used for rotating G. By changing gear head, one could obtain various rotating speeds. The progress of the polymerization was recorded by the oscillograph. After a given time interval, a small amount of methyl alcohol was distilled into the reaction vessel and the reaction was terminated. The contents of the reaction vessel were transferred to a large amount of methyl alcohol containing antioxidant (4,4'-thiobis-6-tert-butyl-3-methylphenol). The recovered polymer was washed with methyl alcohol and dried under reduced pressure. The intrinsic viscosity was measured at 30°C in toluene.

RESULTS

1. R_{po}, Y, and Effect of Stirring.

In Figure 2 the conversion-time curves for various initial catalyst concentrations $[C]_o$ are shown. The initial rate of polymerization R_{po} was very large and when $[C]_o$ was 2.20 mmole/l., the polymerization went to completion within ca. 10 sec. However, the rate decreased rapidly towards the end, and if $[C]_o$ was below a critical value the polymerization stopped before all monomers were consumed. This saturation phenomenon has been described in earlier chapters. In the vacuum system, however, the catalyst concentration required to obtain the same conversion under comparable conditions was only one fourth as much as that

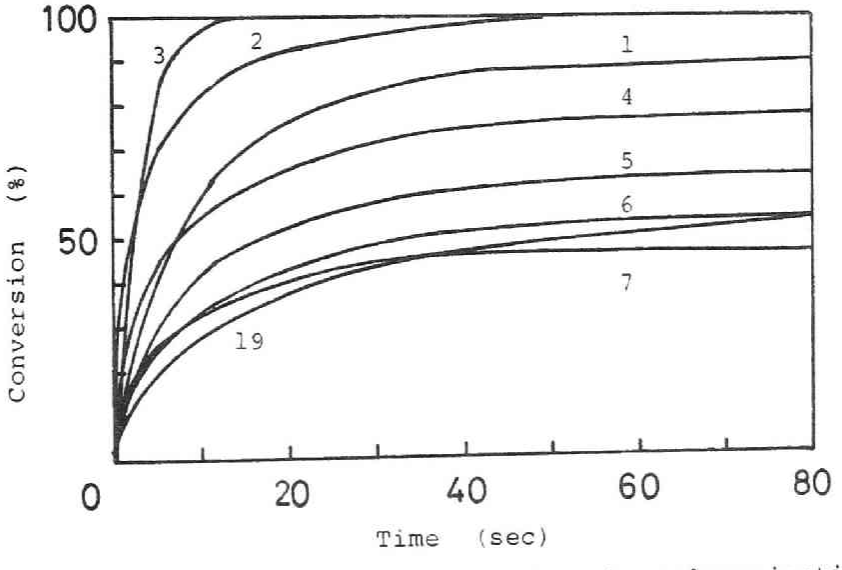

Fig. 2. Conversion-time curves for the polymerization of CPD with $TiCl_4$-TCA in toluene at -75°C. $[M]_o$ 0.45 mole/l. $[C]_o$; (mmole/l) (3) 2.20, (2) 1.53, (1) 1.17, (4) 0.94, (5) 0.62, (6) 0.47, (19) 0.46, (7) 0.36.

with the usual technique. The extremely large rate of polymerization and the saturation phenomenon, i.e. the presence of the final conversion (Y), clearly indicate the non-sationary state concentration of active species coupled with an extremely fast initiation reaction.

Figure 3 shows the relationship between $[C]_o$ and Y or R_{po}. Both Y and R_{po} increased monotonously as $[C]_o$ increased.

At constant $[C]_o$ the initial monomer concentration $[M]_o$ was also changed. In this case the conversion-time curve similar to that shown in Figure 2 was obtained. The influence of $[M]_o$ on Y and R_{po} is shown in Figure 4. As was found previously,[11] Y decreased as $[M]_o$ increased but R_{po} increased with increasing

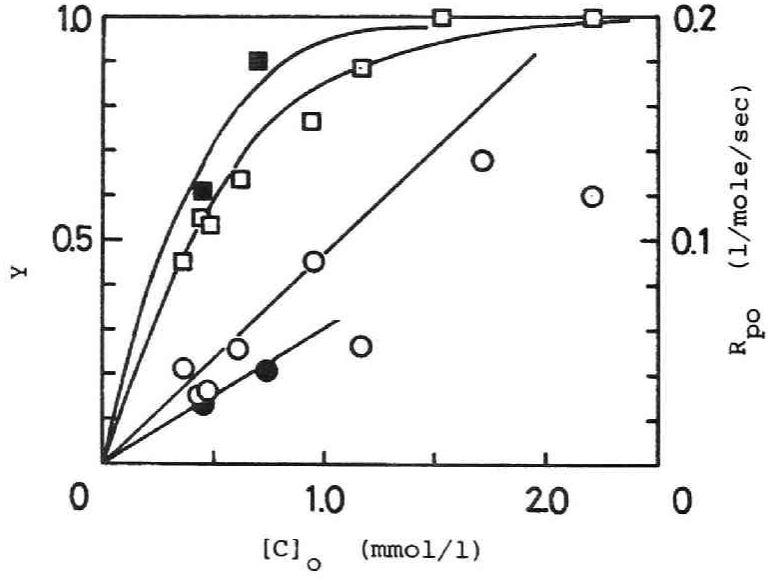

Fig. 3. Relationship between $[C]_o$ and Y (□,■) or R_{po} (○,●). (○,□); $[M]_o$ 0.455 mole/l. (●,■); $[M]_o$ 0.185 mole/l.

$[M]_o$.

As the initial rate is very large in the present system, the stirring of the polymerization mixture is expected to affect the polymerization in some way. In fact the agitation of the system influenced the conversion, as shown in Figure 5. As the rotating speed increased, the rate and the final conversion Y increased. In addition, at a slow stirring speed (below 300 rpm) an induction period of the polymerization was observed. The induction period is supposedly the time required for the catalyst solution to diffuse in the polymerization mixture. However, above 300 rpm the induction period disappeared and the curves at 360 rpm and 240 rpm are in close coincidence. Therefore, if agitation speed exceeds 300 rpm, the influence of stirring on polymerization

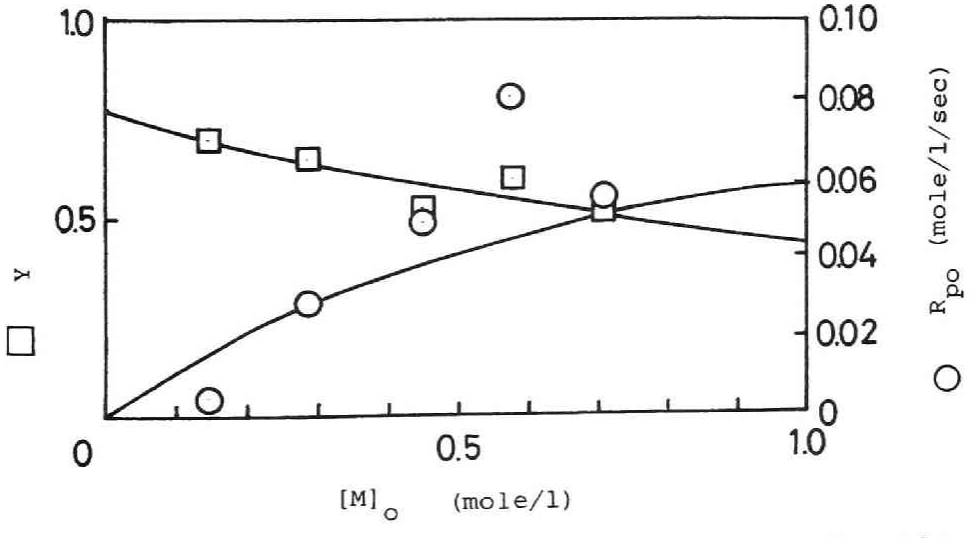

Fig. 4. Relationship between $[M]_o$ and Y (□) or R_{po} (○). $[C]_o$ 0.36 mmole/l.

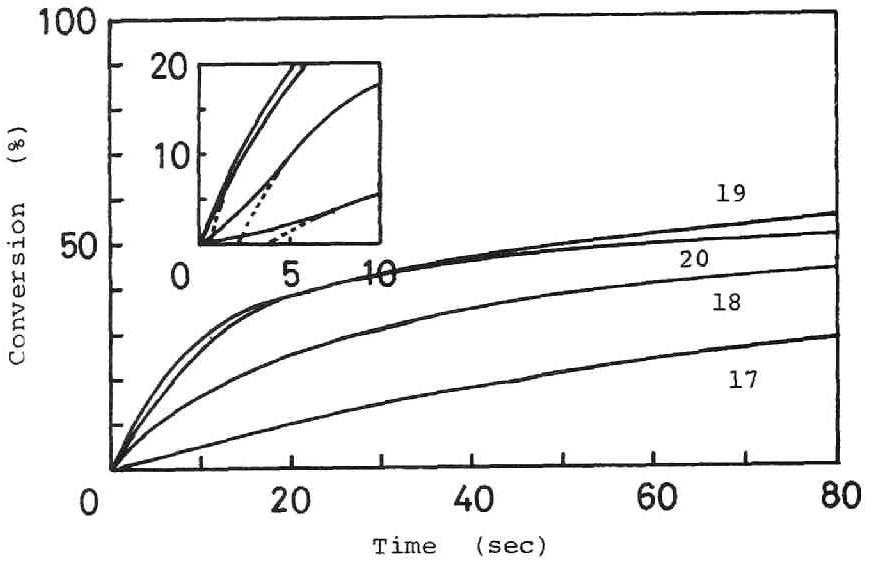

Fig. 5. Influence of stirring speed on polymerization. $[M]_o$ 0.45 mole/l, $[C]_o$ 0.44 mmole/l. Stirring speed; (17) 100 rpm, (18) 144 rpm, (20) 240 rpm, (19) 360 rpm.

rate is insignificant. The present experiments were all conducted under these conditions.

The temperature rise in these experiments was not so large (ΔT = ca. 10°C at $[M]_o$ = 0.454, 100 % conversion). The influence of temperature rise at least on the initial rate can be ignored and the effect on the final conversion might be of minor importance.

All the polymerization data are collected in Table I.

2. Determination of Rate Constants.

By using the kinetics developed in the previous section, the propagation rate constant (k_2) as well as the unimolecular

TABLE I

Polymerization Data of CPD with $TiCl_4$–TCA in Toluene

No.	Temp. °C	$[M]_o$ mole/l	$[C]_o$ mmole/l	RS[a] rpm	t_i[b] sec	R_{po} mole/l/sec	Y	k_2 l/mole/sec	k_5 sec^{-1}
1	-73	0.45	1.17	——	0	0.053	0.90	165	——
2	-69	0.45	1.53	——	0	0.13	1.00	320	——
3	-75	0.45	2.2	——	0.1	0.12	1.00	200	——
4	-75	0.45	0.94	——	0	0.093	0.76	360	0.140
5	-75	0.45	0.62	——	0	0.051	0.63	300	0.114
6	-77	0.45	0.46	——	0	0.032	0.53	250	0.093
7	-77	0.45	0.36	——	0	0.044	0.46	440	0.156
8	-76	0.18	0.72	——	0	0.044	0.91	420	0.099
9	-76	0.29	0.64	——	0.3	0.038	0.81	280	0.076
10	-76	0.59	0.60	——	0	0.086	0.84	450	0.082
11	-71	0.88	0.82	——	1.0	0.12	0.89	375	0.060
12	-73	0.28	0.38	——	0	0.025	0.58	325	0.107
13	-77	0.57	0.36	——	0	0.078	0.53	675	——
14	-76	0.71	0.37	——	0	0.053	0.44	400	0.128
15	-77	0.14	0.35	——	0	0.0034	0.61	83	——
16	-77	0.18	0.44	——	0	0.028	0.61	430	0.160
17	-75	0.45	0.44	100	3.4	——	0.33	——	—
18	-75	0.45	0.43	144	2.4	——	0.44	——	——
19	-75	0.45	0.44	360	0	0.030	0.58	250	0.082
20	-76	0.45	0.45	240	0.3	——	0.50	——	——

[a] Rotating speed of agitation. For No. 1 – 16, RS was around 400 rpm.

[b] Induction period.

termination rate constant (k_5) can be derived.

Determination of k_2. There are two methods for calculating k_2, i.e., from R_{po} only and from both R_{po} and Y.

First, according to eq. (10) we obtain k_2 and k_1'/k_1 from the linearity of the $[M]_o/R_{po}$ versus $[M]_o$ plot. In Figure 6 the plot of $[M]_o/R_{po}$ versus $[M]_o$ is shown.

The R_{po} values observed at various $[M]_o$ and $[C]_o$ were converted into the values at $[C]_o$ = 0.35 mmole/l according to eq. (9) and plotted in Figure 6. The reproducibility of R_{po} is not very good, and the experimental values in Figure 6 are somewhat scattered, but a straight line can be drawn. From the intersection and the tangent of the line, the following values were obtained.

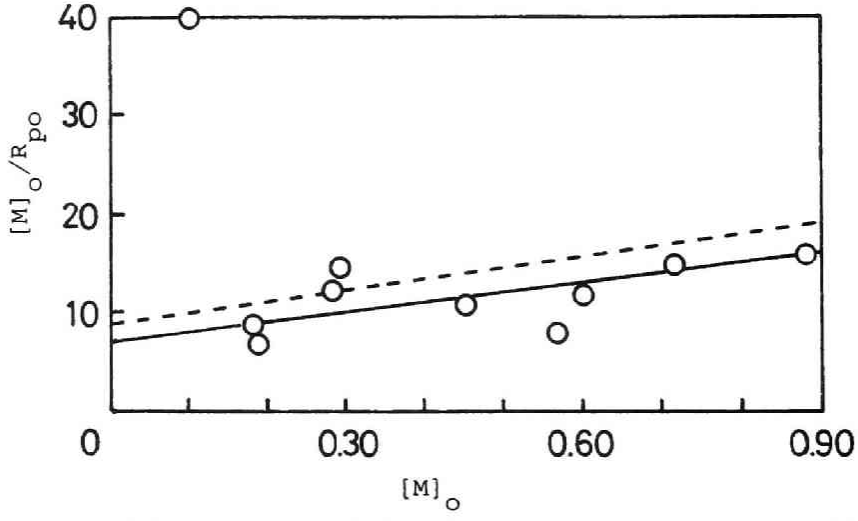

Fig. 6. $[M]_o/R_p$ vs. $[M]_o$ plots according to eq. (10). (——); k_2 = 410 l/mole/sec, k_1'/k_1 = 1.43 l/mole. (----); k_2 = 350 l/mole/sec, k_1'/k_1 = 1.41 l/mole.

$$k_2 = 410 \text{ l/mole/sec} \qquad (15)$$

$$k_1'/k_1 = 1.43 \text{ l/mole} \qquad (16)$$

Secondly, according to eq. (14), the linearity of the $1/\ln(1 - Y)$ versus $[M]_o$ plot gives k_5/k_2 and k_1'/k_1. Plot of $1/\ln(1 - Y)$ versus $[M]_o$ is shown in Figure 7.

The solid line gives

$$k_5/k_2 = 3.0 \times 10^{-4} \text{ mole/l} \qquad (17)$$

$$k_1'/k_1 = 1.41 \text{ l/mole} \qquad (18)$$

In Figure 8 the plot according to eq. (13) is shown. The solid line in the figure is the theoretical one calculated by using

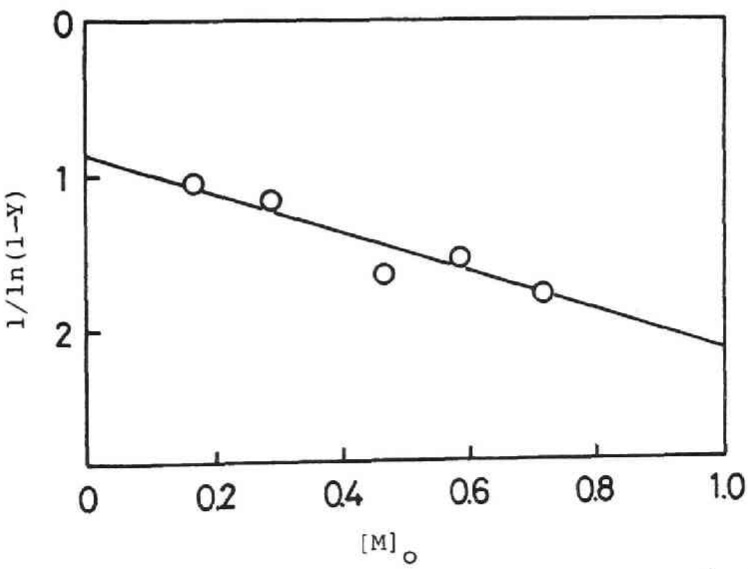

Fig. 7. Plot of $1/\ln(1-Y)$ vs. $[M]_o$. (——); $k_5/k_2 = 3.0 \times 10^{-4}$ mole/l, $k_1'/k_1 = 1.41$ l/mole.

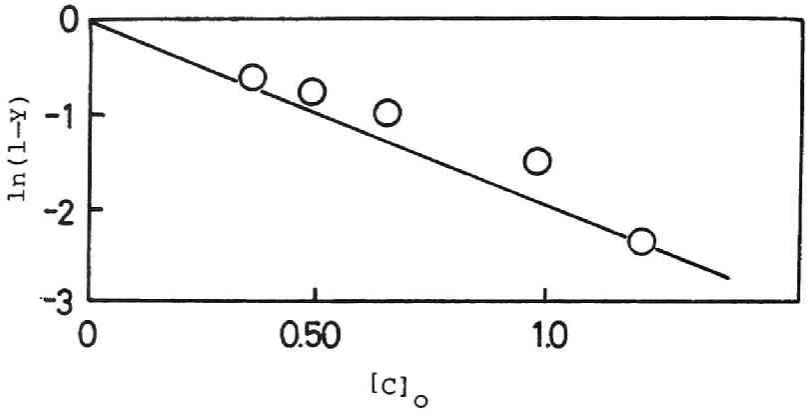

Fig. 8. Plot of ln(1−Y) vs. $[C]_o$. (——); $k_5/k_2 = 3.0 \times 10^{-4}$ mole/l, $k_1'/k_1 = 1.41$ l/mole.

the values of eqs. (17) and (18). The rate constant ratio k_1'/k_1 was given by the usual technique as 1.47 l/mole.[11] The k_1'/k_1 values so far obtained are all in close agreement. So, the values 1.4 was chosen for k_1'/k_1 and then from eq. (9) the propagation rate constant k_2 at various $[M]_o$ and $[C]_o$ was calculated. The rate constants obtained in this way are collected in Table I. An algebraic mean of k_2 values for seventeen experiments gave k_2 = 340 l/mole/sec and standard deviation (SD) = 132. The values lying outside the SD (expt. 1, 3, 13, 15) were omitted and the rest averaged to give

$$k_2 = 350 \pm 71 \text{ l/mole/sec} \qquad (19)$$

The k_2 value determined from Figure 6 and given in eq. (15) is equal to this value [eq. (19)] within the range of experimental error. Thus the propagation rate constants from two different

plots coincide reasonably. In Figures 3, 4, and 6 the theoretical curves calculated by using these rate constants are shown. The agreement between the observed and the calculated points is not completely satisfactory on a quantitative level, but the agreement is good enough for the semi-quantitative discussion.

Determination of k_5. By use of k_2 values in Table I, the termination rate constant k_5 can be calculated according to eq. (12). The k_5 thus obtained are also tabulated in Table I and a mean value for k_5 is

$$k_5 = 0.11 \pm 0.06 \text{ sec}^{-1} \qquad (20)$$

Now the time course of the polymerization was followed by using eq. (11), and the k_5 value was estimated by the curve-fitting method. As for the polymerization 6, the experimental result (the solid line) and the theoretical lines (the dotted lines) were plotted in Figure 9. In this case the theoretical curve which agrees with the experimental value at the final conversion should be

$$\ln([M]_o/[M]_t) = 0.62(1 - e^{-k_5 t}) \qquad (21)$$

The dotted lines 1, 2, and 3 correspond to k_5 = 0.16, 0.12, and 0.09, respectively. The larger the k_5 value, the better the coincidence at the initial stage and the worse at the intermediate stage; if k_5 is small, the converse is true. From Figure 9 the best fit of k_5 was 0.12, so it is safe to say that k_5 of 0.11 sec^{-1} which came from other kinetics can also account for the

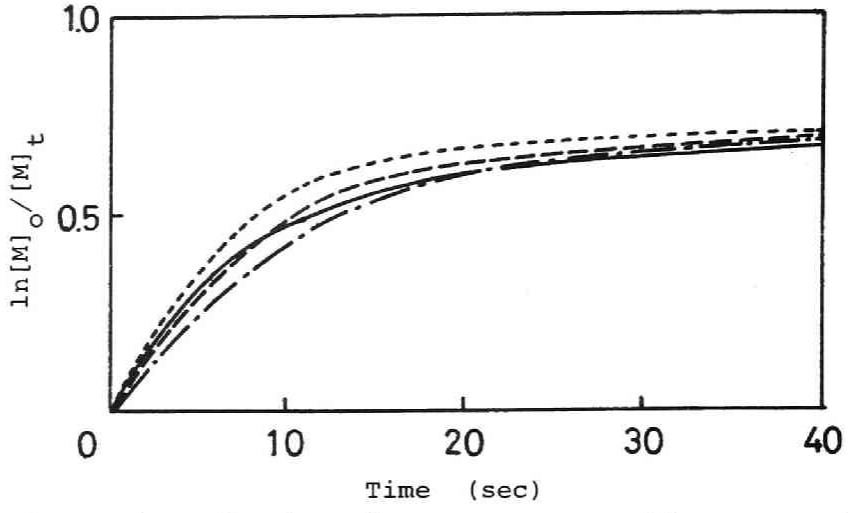

Fig. 9. Polymerization time courses according to eq. (11). (———); observed. (---); k_5 = 0.156, k_2 = 440. (— —); k_5 = 0.120, k_2 = 340. (—·—·); k_5 = 0.090, k_2 = 250

time course of the polymerization. But the agreement of the theoretical with the experimental data was not sufficiently good even when the best value of k_5 was used. On the other hand, by using eq. (21), k_5 can be calculated from the experimental curve of Figure 9. The k_5 values thus calculated as a function of time t are shown in Table II. These pseudo first-order rate constants k_5 were within the limit of the value [see eq. (20)] but decreased monotonously with time and could not be regarded as a constant.

The nature of the termination rate constant k_5 is not clear at the present (see, however, the Discussion). But since the k_2 values were obtained without the k_5 values, the validity of the k_2 values is not influenced by the ambiguity of the k_5 value.

TABLE II

Change of k_5 with Time

Time, sec	k_5, sec^{-1}
1	0.175
2	0.150
3	0.140
5	0.131
6	0.121
8	0.114
10	0.106
15	0.103
20	0.093_5
25	0.086_4
30	0.085_6

DISCUSSION

In the preceding section some rate constants and their ratio were determined.

$$k_1'/k_1 = 1.4 \text{ l/mole}$$

$$k_2 = 350 \pm 70 \text{ l/mole/sec}$$

$$k_5 = 0.11 \pm 0.06 \text{ sec}^{-1}$$

TABLE III

Propagation Rate Constant (k_2) in Cationic Polymerization of Vinyl Monomers

Monomer	Catalyst	Solvent	Temp. °C	k_2 1/mole/sec	Ref.
Styrene	H_2SO_4	$(CH_2Cl)_2$	25	7.6	3,4
"	$HClO_4$	"	30	17.0	5
"	$SnCl_4$	"	"	0.42	7
"	I_2	"	"	0.0037	2
"	$BF_3 \cdot O(C_2H_5)_2$	C_6H_6	"	0.17	18
"	$ReCl_5$	'	20	1.59	10
Isobutyl vinyl ether	I_2	CCl_4	30	0.083	2
"	$BF_3 \cdot O(C_2H_5)_2$	$n\text{-}C_6H_{14}$– $C_6H_5CH_3$	-40	7.7	8
Isobutene	$AlBr_3$–$TiCl_4$	$n\text{-}C_7H_{16}$	-14	6.3×10^3	9
α-Methyl-styrene	γ-radiation	bulk	30	3×10^6	19
Cyclopenta-diene	"	"	-78	5.8×10^8	20
"	$TiCl_4$-TCA	$C_6H_5CH_3$	-75	350	this work

For the propagation rate constant in cationic polymerization of vinyl monomers the present data are compared with some literature values in Table III. Except for the radiation-induced polymerization in which free ions are involved, the k_p value of CPD is comparatively large, and it is exceded only by the k_2 for the IB–$AlBr_3$-$TiCl_4$–n-heptane system investigated by Chemelir and Marek.[9] Thus the high polymerizability of CPD in cationic polymerization is interpreted at least partly in terms of the large k_2 value. However the value 350 l/mole/sec is much smaller than k_2 for the radiation-induced polymerization of CPD. So it is probable that the $TiCl_4$-TCA-induced polymerization proceeds by an ion-pair mechanism as has been supposed from the structure of polycyclopentadiene.[16,17] Furthermore according to the study of the polymer structure by Aso et al.,[17] the k_2 value obtained here is composite, i.e., k_2 of 1,2-addition (ca. 55 %) and 1,4-addition. Since the effect of polymerization conditions on the propagation mode is not significant,[17] the validity of k_2 values is not affected by the polymerization conditions.

The termination rate constant, 0.11 sec^{-1}, is very large compared to that of styrene–H_2SO_4–$(CH_2Cl)_2$ (0.0067 sec^{-1}), but the ratio k_5/k_2 is ca. 10^{-3} in either case. In the cationic polymerization the termination reaction cannot be ignored, whereas the mechanism of the termination reaction has not been made clear. In the kinetic treatment of the present system the unimolecular termination reaction was temporarily assumed, but as in Table II, the termination reaction does not seem to be completely unimolecular. As an alternative possibility for

the termination reaction, the termination by monomer [eq. (22)] can be put forward in analogy with the reaction (1), which competes with the initiation reaction and can be regarded as a kind of termination reaction.

$$P_r^* + M \xrightarrow{k_5'} P \qquad (22)$$

If the reaction (22) alone represents the termination reaction, we obtain

$$-d[M]/dt = (k_2[P^*]_o - k_5[M]_o)[M]_t + k_5[M]_t^2 \qquad (23)$$

$$Y = \frac{k_2}{k_5} \frac{k_1}{k_1 + k_1'[M]_o} \frac{[C]_o}{[M]_o} \qquad (24)$$

However the plots according to eqs. (23) or (24) do not agree with the experimental findings, so the reaction (22) as a sole termination reaction cannot explain the reaction kinetics. Again alternatively, the termination by residual water in the system would be more feasible, that is

$$P_r^* + H_2O \xrightarrow{k_5''} P_r \qquad (25)$$

Since some water (of the order of several millimoles per liter) is usually present, which is much higher than P_r^*, the polymerization kinetics seems to be explained by assuming a first-order termination reaction, although the termination reaction is actually second-order as shown by eq. (25).[11] In the present case it was difficult to measure the residual water concentration, so

a quantitative test of eq. (25) was not done. However, in analogy with Chemelir and Marek,[9] who investigated the isobutene polymerization by a similar technique, 10^{-3}–10^{-1} mmole/l is suggested for the residual water concentration; this is comparable to the concentration of active species or the initiator concentration. In any event we cannot treat the termination reaction fully quantitatively at present and therefore cannot draw any definite conclusions about the reaction mechanism. All the reactions mentioned above may be involved in the termination reaction in this system, and only apparent unimolecular termination constants ($k_{5,app}$) could have been obtained:

$$k_{5,app} = k_5 + k_5'[M] + k_5''[H_2O]$$

so it is possible that the diminution of k_5 value with time as shown in Table II is due to the consumption of the monomer and the residual water resulting from the reactions (24) and (25).

The present method for obtaining the propagation rate constant has been developed on the basis of the kinetics involving the fast initiation reaction with some termination. Since the polymerization of cyclic dienes is, so far as has been investigated, accompanied by a fast initiation reaction under a variety of conditions, the present method promises the determination of the propagation rate constant under various sets of combinations of cyclic diene–catalyst–solvent–temperature. The experimental method established in this investigation may be applied to other polymerization systems which show a non-stationary state character

resulting from a very fast initiation reaction with some termination reaction. The propagation rate constants in cationic polymerization will be determined in a variety of systems according to the present method.

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Chapter 9

Polymerization with Perchloric Acid and Acetyl Perchlorate Catalysts

INTRODUCTION

For a long time, inorganic protonic acids have been known to initiate the cationic polymerization of vinyl monomers, though only a few papers have been published on the kinetics of these polymerizations. Pepper et al. reported the polymerization of styrene by sulfuric acid[1] and by perchloric acid.[2] A termination reaction occurs in the styrene-H_2SO_4 system, but does not occur in the styrene-$HClO_4$. The latter is a transfer-dominated living-polymerization system. In the former the stationary state about the concentration of active species was not established during the polymerization (a typical example of non-stationary state cationic polymerization). The kinetics of these polymerizations is apparently simple and the polymerization is believed to proceed via carbonium ions, while Plesch et al[3] claimed that the polymerization of styrene by perchloric acid is not cationic and the ester is an active species.

In the preceding chapter the kinetics of the polymerization of cyclopentadiene (CPD)–$TiCl_4$-trichloroacetic acid (TCA) system was investigated under a vacuum condition and the propagation rate constant was successfully determined by the non-stationary

state kinetics, which was developed by modifying the kinetics proposed for the styrene–H_2SO_4 system.[1] The present work was undertaken to determine the propagation rate constant (k_2) for the polymerization of CPD by $HClO_4$ and acetyl perchlorate ($AcClO_4$), which are different in nature from $TiCl_4$-TCA. Both initiators have a common anionic moiety, so that the same k_2 value should result if the non-stationary state kinetics can be applied to the present catalysts. Despite the complex behaviour suggested in preliminary reports for the $HClO_4$-induced polymerization of styrene,[4] the non-stationary state kinetics to determine the k_2 value was tested for the $HClO_4$- or $AcClO_4$-induced polymerization of CPD in this chapter.

EXPERIMENTAL

Materials

Purifications of CPD, toluene and methylene chloride were already described in earlier chapters. Anhydrous perchloric acid solution in methylene chloride or in toluene was prepared by essentially the same method as that of Pepper et al.[5] Acetyl perchlorate was synthesized by the reaction of silver perchlorate with acetyl chloride in methylene chloride and the concentration was determined spectroscopically according to the method of Masuda.[6] The concentrated solutions of $HClO_4$ and $AcClO_4$ in CH_2Cl_2 were stored in a refrigerator, and were diluted on each use. The period of storage did not exceed a month. The catalyst solutions in toluene seemed not to be stable, so that the $HClO_4$ in toluene was prepared on each use. The $AcClO_4$ in toluene was

most unstable and the polymerization by $AcClO_4$ in toluene was not carried out.

Procedures

The polymerizations were carried out under a dry nitrogen atmosphere as described in Chapter 6. The polymerization rate in methylene chloride was quite large, so the polymerization by $AcClO_4$ was conducted in a mixture of toluene and methylene chloride. Methanol-insoluble products were recovered and dried under vacuum. Viscosity was measured in toluene at 30°C.

RESULTS

1. Polymerization by Perchloric Acid.

Figure 1 shows the time-conversion curves of the polymerization of CPD by $HClO_4$ in toluene at -78°C. At first, the rate was extremely large but decreased progressively, and soon after that, the polymerization stopped when unreacted monomers still existed. This behaviour could be reasonably explained by assuming a very rapid initiation and a propagation accompanied by some terminations, analoguous to the styrene-H_2SO_4 system.[1] The relationship between the final conversion (Y_∞) and the initial catalyst concentration (C_o) or the initial monomer concentration (M_o) is illustrated in Figures 2 and 3, respectively. In Figure 2, the plot of $\ln 1/(1-Y_\infty)$ against $[C]_o$ forms a straight line, which crosses the abscissa at C_o = 1.0 mmole/l. This anomaly could have arisen from the presence of impurities to destroy the catalyst such as water. Y_∞ is independent of M_o as demonstrated

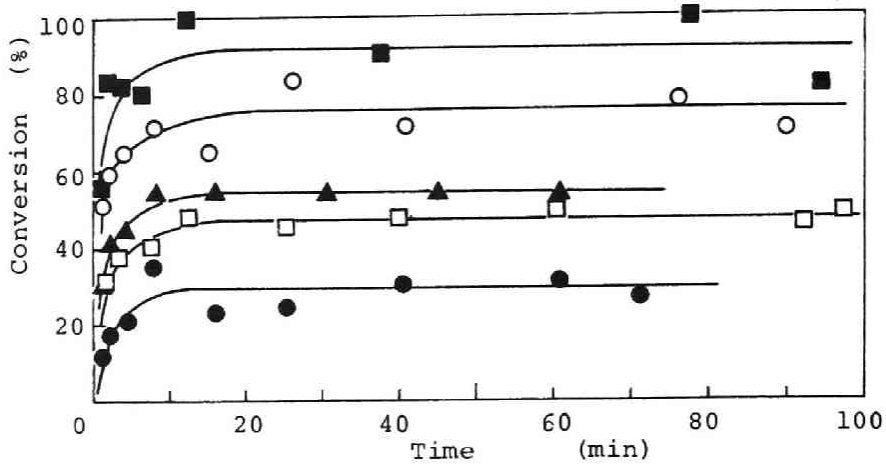

Fig. 1. Conversion-time curves for the polymerization of CPD with perchloric acid. Solvent toluene, Temp. -78°C, M_o 1.3 mole/l, C_o (mmole/l) ● 5.0 □ 8.6 ▲ 8.8 ○ 11 ■ 14.

in Figure 3, which is differnt from the result obtained in the polymerization of CPD by $TiCl_4$-TCA[7,8] and the same as styrene-H_2SO_4 system.[1]

The nuclear magnetic resonance spectra of the polymers indicated that about 15 % of the olefinic protons were lost, which is larger than the values found for the polymers obtained by Friedel-Crafts catalysts. The reaction of olefinic double bond in the polymers may have been important under the present conditions. Thus a small amount of insoluble polymers was always formed. These polymers seemed to be crosslinked. The crosslinking reaction might be important with the present catalyst. Nevertheless, the ratio of 1,2 structure and 1,4 structure determined by nuclear magnetic resonance spectroscopy and the intrinsic viscosity of the polymers (0.1 to 0.4) were almost the same as those for the polymers obtained with Friedel-Crafts halides.[7,9]

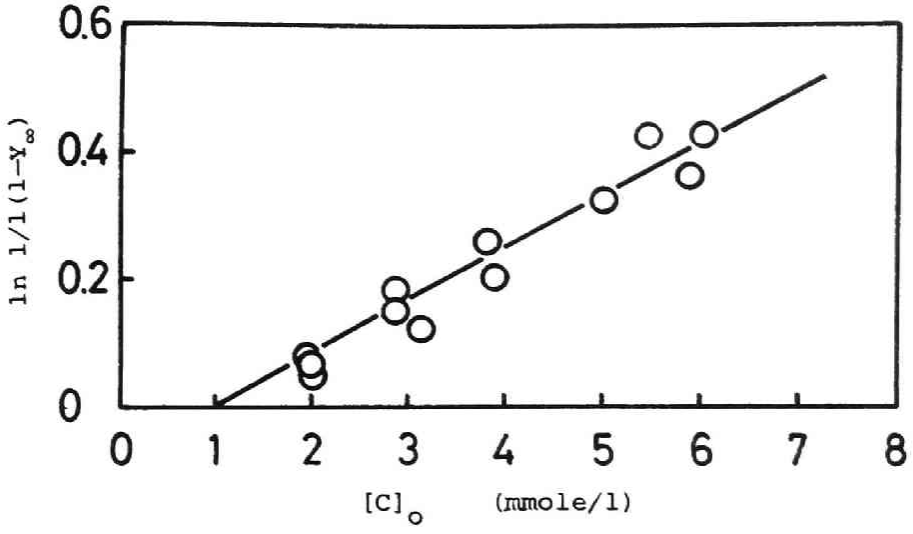

Fig. 2. Relationship between ln $1/(1-Y_\infty)$ and $[C]_o$. Polymerization solvent methylene chloride, Temp. -78°C, M_o 1.3 mmole/l.

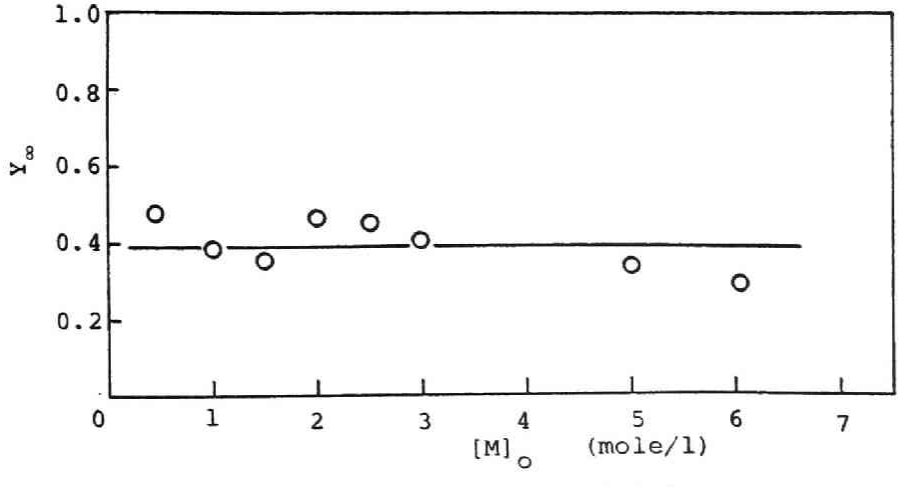

Fig. 3. Relationship between Y_∞ and $[M]_o$. Polymerization solvent toluene, Temp. -78°C, C_o 13 mmole/l.

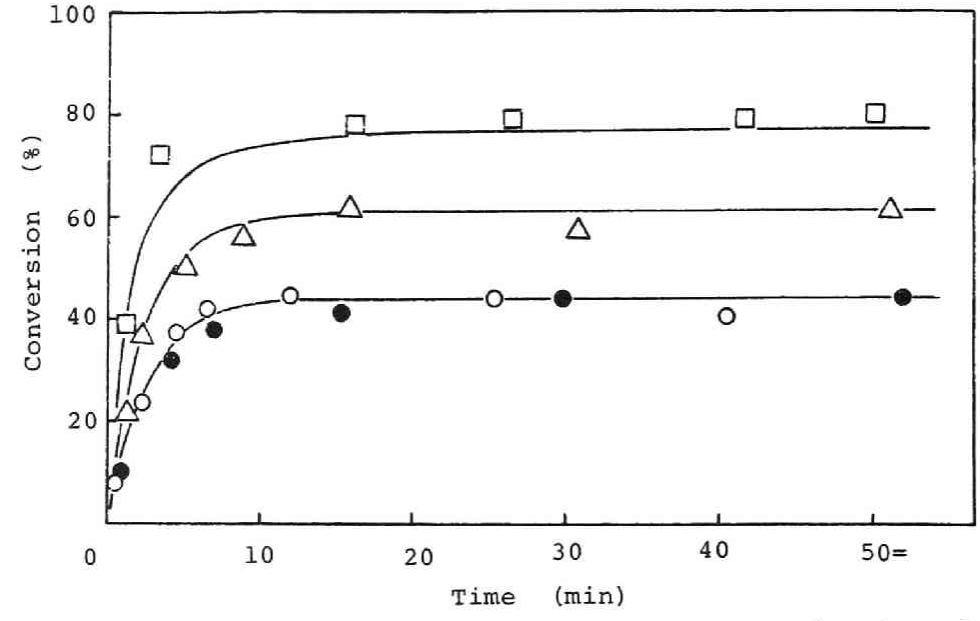

Fig. 4. Time-conversion curves for the polymerization of CPD with acetyl perchlorate. Temp. -78°C, M_o 1.3 mole/l, C_o (mmole/l) ○ 3.0 ● 3.0 △ 4.9 □ 7.3.

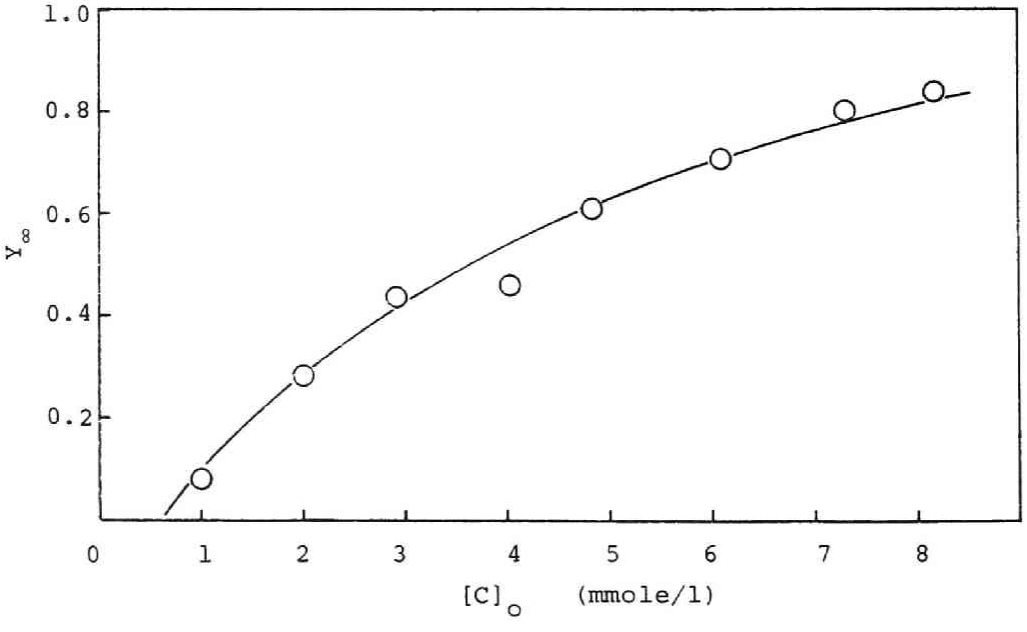

Fig. 5. Relationship between Y_∞ and C_o for the polymerization of CPD with acetyl perchlorate. Temp. -78°C, M_o 1.3 mole/l.

2. Polymerization by Acetyl Perchlorate.

The time-conversion curves for the polymerization of CPD by $AcClO_4$ are shown in Figure 4. The behaviour is as a whole the same as that shown in Figure 1 for $HClO_4$. Duplicate polymerizations under the same conditions (○ and ●) demonstrated the good reproducibility of the polymerization rate. The change of Y_∞ with C_o is shown in Figure 5. Y_∞ increased monotonously with increasing C_o and the ln $1/(1-Y_\infty)$ *vs.* $[C]_o$ plot forms a straight line similar to Figure 2. The properties of the polymer were essentially the same as those of the polymer produced by $HClO_4$.

3. Determination of the Propagation Rate Constants.

The kinetic behaviours described in Subsections 1 and 2 (very fast initial rate of polymerization, saturation of conversion and dependencies of final yield on C_o and independence on M_o) clearly indicate the resemblance to those of styrene–H_2SO_4 system, and are successfully interpreted by the non-stationary state kinetics proposed by Pepper et al.[1] The elementary reactions proposed by Pepper for his system could be applied to the present system, and are described in Section 1.1 of Chapter 1 as equations (1) to (5). Based on these elementary reactions, the following equations were derived for Y_∞ and Y_t:

$$\ln\left(\frac{1}{1 - Y_\infty}\right) = \frac{k_2}{k_5} \cdot C_o \qquad (1)$$

$$\ln\left(\frac{1}{1 - Y_t}\right) = \frac{k_2}{k_5} \cdot C_o\left(1 - e^{-k_5 \cdot t}\right) \qquad (2)$$

where Y_t means the yield of polymer at time t. According to eq. (1), rate constant ratio (k_2/k_5) is calculated from the linear plot of $\ln 1/(1-Y_\infty)$ *vs.* C_o. k_5 value was determined by testing different k_5 values so that the best fit of the observed time-conversion curve with the $Y_t \sim t$ curve calculated using eq. (2) is obtained. Thus the propagation rate constant k_2 is also determined from (k_2/k_5) and k_5.

The rate constants evaluated by this means are shown in Table I. The solid lines in Figures 1, 4 and 5 are the calculated ones using these rate constants. The agreement of the experimental points with the calculated curves is satisfactory for the polymerization technique employed here (not a vacuum technique). Figure 3 shows the independence of Y_∞ on M_o in accordance with eq. (1). All these facts give a support for the present kinetic treatment and the calculated rate constants.

DISCUSSION

The propagation and termination rate constants in the polymerization of CPD with $HClO_4$ and $AcClO_4$ were estimated using a non-stationary state kinetics. With these catalysts, the side reaction, *i.e.*, the reaction of a catalyst with two monomers leading to the formation of inactive compound as described in Section 1.1 of Chapter 1, was not included. This type of reaction would have resulted in the dependence of final yield on M_o, which

was not observed. This is consistent with the fact that $HClO_4$ or $AcClO_4$ does not form the ferrocene type complex with CPD.

The values of k_2 for CPD-$HClO_4$ and CPD-$AcClO_4$ systems are equal within experimental errors and much smaller than that of CPD-$TiCl_4$-TCA system as can be seen from Table I. For the cationic polymerization of styrene, protonic acids showed higher potency than Friedel–Crafts halides, but for CPD the reverse is true. This is estimated to be due to the difference of the transition states of styryl and cyclopentenyl growing ion-pair, but the details could not be discussed without more results. Further this might be concerned with the complicated nature of the active species in cationic polymerization as exemplified in the styrene-$HClO_4$ system.[2,3,4)]

As mentioned earlier, styrene-$HClO_4$ system is a transfer-dominated living-polymer system at ambient temperatures,[2)] but at lower temperatures some termination process does exist.[4)] Though the complete interpretation of this temperature effect has not been furnished, Pepper et al. considered that at least two kinds of active species are involved in the styrene-$HClO_4$ system, ion pair being predominant at ambient temperatures and free ions at lower temperatures.[4)] For the polymerization of CPD at low temperatures, the k_2 values are much smaller than that for the free cation of CPD (5.8×10^8 l/mole/sec).[12)] Hence the k_2's of CPD in Table I are no doubt concerned with ion-pair polymerizations. The identity of k_2's for CPD-$HClO_4$ and for CPD-$AcClO_4$ under the present conditions leading to ion-pair polymerizations, certifies the validity of the present kinetic treatment. In

TABLE I

Propagation and Termination Rate Constants

Monomer	Initiator	Polymerization Solvent	Polymerization Temp.(°C)	k_2 (l/mole/sec)	k_5 (sec^{-1})	Ref.
CPD	$HClO_4$	toluene	-78	0.83	0.008	this work
"	"	CH_2Cl_2	"	6.7	0.057	"
"	"	tol.-CH_2Cl_2[a]	"	0.93	0.0063	"
"	CH_3COClO_4	"	"	0.99	0.0052	"
'	$TiCl_4$-TCA[b]	toluene	-75	350	0.11	5
Styrene	H_2SO_4	$(CH_2Cl)_2$	25	7.6	0.0067	1
"	$HClO_4$	"	30	17.0	——	2
"	$SnCl_4$	"	"	0.42	——	10
"	$BF_3 \cdot OEt_2$	benzene	"	0.18	——	11

[a] Toluene (76 vol.%), methylene Chloride (14 vol.%), monomer (10 vol.%).

[b] Trichloroacetic Acid.

addition, the k_2 in toluene–methylene chloride mixture is the intermediate value between those in toluene and methylene chloride, as expected. For the above conclusion to be firm, it should rest not only on the kinetic basis but also on the chemical or the spectroscopic basis. Further investigations are needed in the future.

To summarize, all the experimental results support the kinetic treatment presented in this chapter and in Chapter 8. The different rate constants for the polymerizations initiated by different catalysts are interpreted in terms of the different influence of the anionic moieties in the propagating ion pairs.

Note Added in Proof: After the study in this chapter was completed, the low temperature polymerization of styrene by $HClO_4$ was reported, see M. De Sorgo, D. C. Pepper, and M. Szwarc, J. C. S. Chem. Commun., 1973, 419.

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Chapter 10

Activation Parameters for the Propagation Reaction by Titanium Tetrachloride-Trichloroacetic Acid

INTRODUCTION

A very large rate of polymerization was observed in the polymerization of cyclopentadiene (CPD) by $TiCl_4$-trichloroacetic acid (TCA) in toluene at -78°C,[1] and the high reactivity of CPD was confirmed in cationic copolymerization (see Part II). The high reactivity of CPD has been explained in terms of a high nucleophilicity of CPD and a high stability of cyclopentenyl cation.[2] In fact, the propagation rate constant determined for CPD–$TiCl_4$-TCA–toluene system is one of the largest ones reported for ion-pair polymerizations.[3]

There have been only a few investigations about activation parameters in cationic polymerization. Kanoh et al.[4] reported that the presence of a counter ion decreases the freedom of internal rotation of the growing end which results in low frequency factor for the propagation with ion-pair mechanism. Recently, this sort of investigation was made for the radiation-induced polymerization of styrene.[5] This system is free-cationic, having a high frequency factor and a low activation energy for the propagation reaction.

In this chapter, the kinetic study was further advanced to determine the activation parameters for the propagation reaction of CPD in the $TiCl_4$-TCA-toluene system, because in non-polar solvents such as toluene, the propagating species were estimated to be ion-pairs and the propagation rate constant was very large for this system as described in Chapter 8. The determination of activation parameters would clarify whether the fast propagation is entropy-controlled or energy-controlled.

EVALUATION AND EXPERIMENTAL

In Chapter 8, the propagation rate constant was determined by two different methods, i.e., the determination from initial rate and that from both initial rate and final yield. The values determined by the two methods agreed well within experimental errors. In this chapter, the propagation rate constant [k_2, from eq. (1)] and the rate constant ratios [k_1'/k_1 and k_5/k_2, from eqs. (1) and (2)] were determined at different temperatures according to the equations:

$$\frac{[M]_o[C]_o}{R_{po}} = \frac{1}{k_2} + \frac{1}{k_2}\frac{k_1'}{k_1}[M]_o \qquad (1)$$

$$-\frac{[C]_o}{\ln(1-Y)} = \frac{k_5}{k_2} + \frac{k_5}{k_2}\frac{k_1'}{k_1}[M]_o \qquad (2)$$

where the notations are the same as those in the kinetic treatment section in Chapter 8. Eqs. (1) and (2) are the same as eqs. (10) and (14) in Chapter 8, respectively. In these equations, $[M]_o$

and $[C]_o$ are known, and R_{po} and Y are experimentally determinable. k_2 and k_1'/k_1 were obtained from the intercept and the slope of the straight line for the plot of $[M]_o \cdot [C]_o/R_{po}$ vs. $[M]_o$ [eq. (1)], while k_5/k_2 and k_1'/k_1 from $-[C]_o/\ln(1 - Y)$ vs. $[M]_o$ plot [eq. (2)].

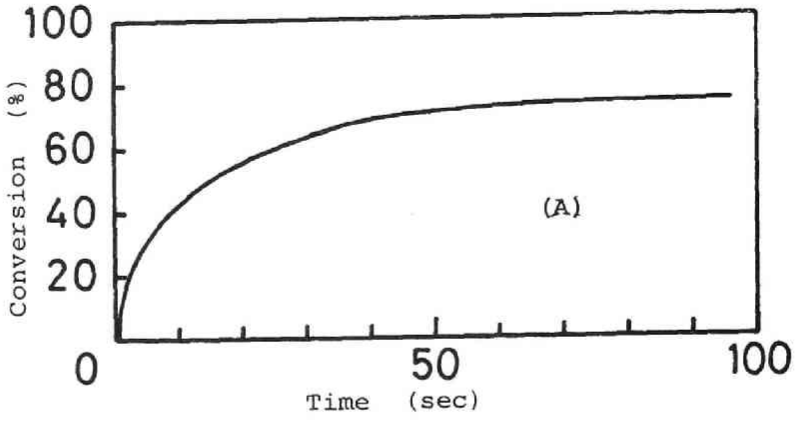
The frequency factor (A_p) and the activation energy (E_p) of the propagation reaction were determined according to the Arrhenius equation.

Experimental techniques were the same as those described in Chapter 8.

RESULTS

The polymerization of CPD by $TiCl_4$-TCA were carried out in toluene at -90°C, -50°C, and -20°C. The initial rate of polymerization was larger at higher temperatures. Typical examples of the time-conversion curves at -90°C and -20°C are shown in Figure 1. The shape of the time-conversion curve is the same as those for the polymerization at -78°C[1] or at -75°C,[3] i.e., a large rate of polymerization at the initial stage and a saturation of conversion at the later stage. However, the initial rate was dependent on the polymerization temperature. The higher the temperature, the larger the rate of polymerization. As can be seen from Figure 1, the rate was so large as the polymerization reached a final yield in a second or two at -20°C.

The plots according to eqs. (1) and (2) are shown in Figures 2 and 3 for the polymerization at 90°C. A similar plot was obtained for the polymerization at -50°C or -20°C. The rate constants determined from these plots are summarized in Table I.



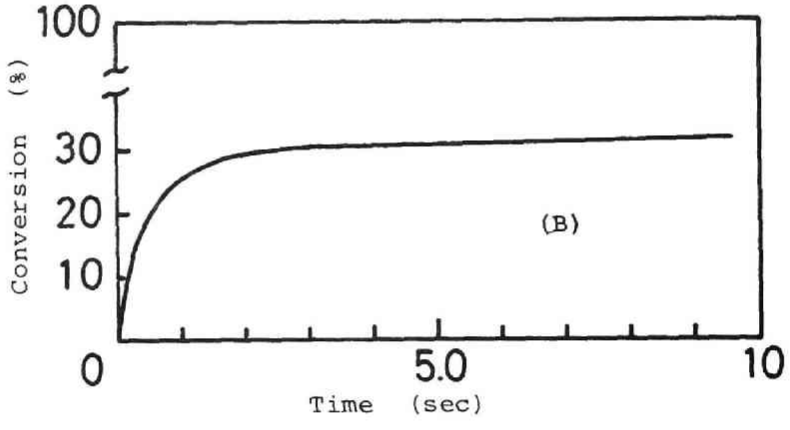


Fig. 1. Conversion-time curves for the polymerization of CPD by $TiCl_4$-TCA in toluene. (A) Polymerization at -90°C, $[M]_o$ 0.68 mole/l, $[C]_o$ 0.56 mmole/l. (B) Polymerization at -20°C, $[M]_o$ 0.84 mole/l, $[C]_o$ 0.47 mmole/l.

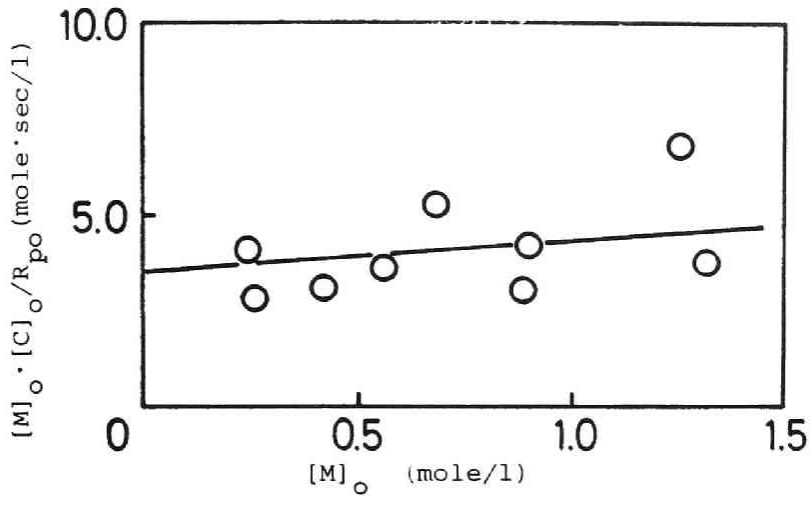


Fig. 2. Plot according to equation (1). Polymerization at -90°C, $[C]_o$ 0.4 – 0.7 mmole/l, Polymerization solvent toluene.

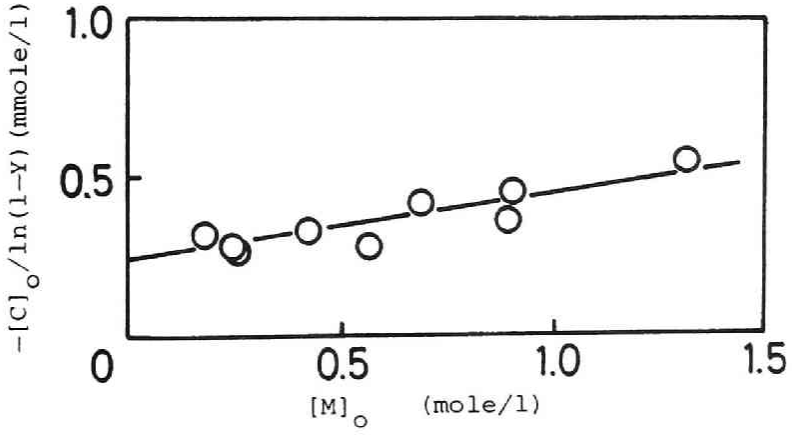


Fig. 3. Plot according to equation (2). Polymerization conditions are the same as in Fig. 2.

TABLE I

Rate Constants Determined for CPD–$TiCl_4$-TCA–toluene at Several Temperatures[a]

Temperature	From eq. (1)		From eq. (2)		k_5[b]
	k_2	k_1'/k_1	k_5/k_2	k_1'/k_1	
°C	l/mole/sec	l/mole	mole/l	l/mole	sec^{-1}
-90	280 ± 60	0.23	0.24×10^{-3}	1.02	0.067
-75	410 ± 80	1.43	0.30×10^{-3}	1.41	0.11
-50	7100 ± 1000	1.36	0.24×10^{-3}	3.58	1.7
-20	12500 ± 4500	14	0.13×10^{-3}	16	1.6

[a] $[C]_o$ 0.3–0.7 mmole/l, $[M]_o$ 0.2–1.4 mole/l.

[b] Calculated from k_2 and k_5/k_2.

k_2 is very large at higher temperatures and at -20°C it exceeded 10^4 l/mole/sec. The rate constant ratio (k_1'/k_1) obtained from eq. (1) were approximately the same order of magnitude as those from eq. (2) except for -90°C. This supports the present kinetic treatment.

The Arrhenius plot of k_2 is shown in Figure 4, which gave the following values as activation parameters:

Frequency factor $\log A_p = 10.0 \pm 1.6$

Activation energy $E_p = 6.0 \pm 1.4$ Kcal/mole.

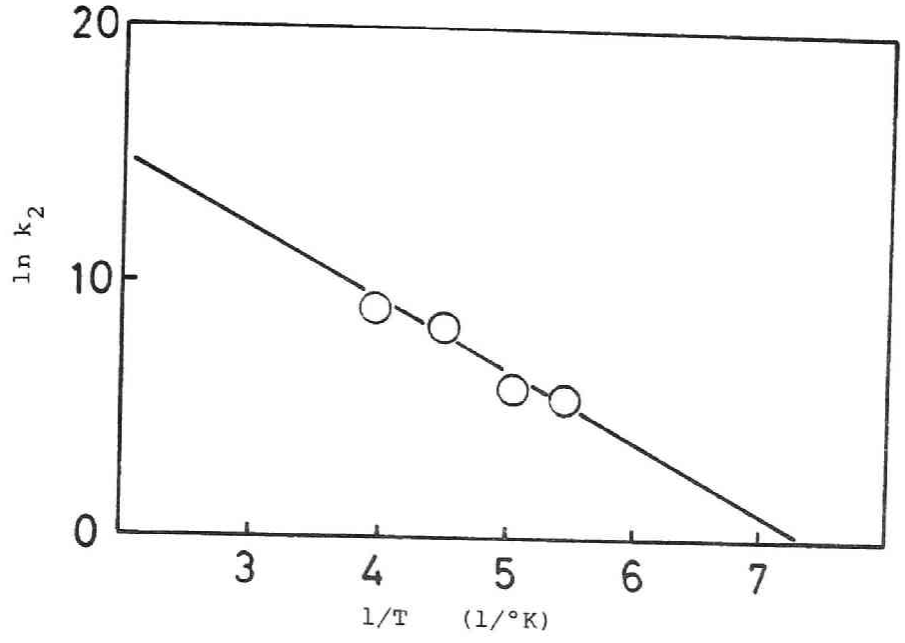


Fig. 4. Arrhenius plot of the propagation rate constant (k_2). The values of k_2 are taken from Table I.

DISCUSSION

The propagation rate constants for CPD are compared with those of styrene and isobutyl vinyl ether in Table II. k_2 values in the radiation-induced polymerization are overwhelmingly larger than those in the catalyst-induced polymerizations. This could be reasonably explained by a high reactivity of weakly solvated or naked free ions involved in the radiation polymerization. Radiation polymerizations of styrene and CPD have been

TABLE II

Propagation Rate Constant (k_2) of Styrene, Isobutyl Vinyl Ether, and CPD in Cationic Polymerization

Monomer	Catalyst	Solvent	Temperature °C	k_2 l/mole/sec	Reference
Styrene	$BF_3 \cdot OEt_2$	C_6H_6	30	0.17	6
"	$HClO_4$	CH_2Cl_2	-80	2.2×10^3	7
"	radiation	bulk	25	2.4×10^6	5
Isobutyl Vinyl Ether	I_2	$(CH_2Cl)_2$	30	6.5	8
"	$C_7H_7^+SbCl_6^-$	CH_2Cl_2	0	4.0×10^3	9
"	radiation	bulk	25	1.2×10^5	10
CPD	$HClO_4$	toluene	-78	0.83	Present thesis
"	"	tol.-CH_2Cl_2 [a]	"	0.93	"
"	CH_3COClO_4	"	"	0.99	"
"	$HClO_4$	CH_2Cl_2	"	6.7	"
"	$TiCl_4$-TCA	toluene	-90	280	"
"	"	"	-75	410	"
"	"	"	-50	7.1×10^3	"
"	"	"	-20	1.25×10^4	"
"	radiation	bulk	-78	5.8×10^8	11

[a] Toluene (76 vol%), CH_2Cl_2 (14 vol.%), Monomer (10 vol.%)

carried out in bulk so that the free ions produced are solvated only weakly. On the other hand, in the bulk polymerization of isobutyl vinyl ether, the free ions may be solvated by the monomer to some extent, which resulted in relatively low k_2 value.[10)]

The polymerizations of isobutyl vinyl ether by carbonium ion salts and of styrene by perchloric acid at -80°C showed large k_2 values among the catalyst-induced polymerizations. These polymerizations were considered to propagate with free ions due to the high polarity of the solvent and the stability of the counter anion. However, k_2 value for the carbonium salt-induced solution polymerization was smaller by almost two orders of magnitude than that of the radiation-induced bulk polymerization. A solvation of the carbonium ions by methylene chloride might have decreased k_2 value.[10,12)]

The polymerization of CPD was carried out in toluene as a solvent, so the contribution of free-cationic species would be negligible. Nonetheless, the k_2 value as large as 10^4 l/mole/sec was obtained at -20°C, which was much larger than expected for ion-pair species. As frequently noted in earlier chapters, this unusually large k_2 value is at least partly due to the high nucleophilicity inherent in CPD and the stability of cyclopentenyl cation. Further to those, the stability of the cation and the counter anion ($CCl_3COO \cdot TiCl_4^-$) contribute to form a loose ion-pair in toluene. A loose ion-pair surely shows high reactivity in ionic polymerization. This point will be more discussed later on.

Activation parameters for the polymerization of CPD are compared with those reported for styrene, isobutyl vinyl ether in Table III. It can be seen from Table III that the activation energy of the propagation of CPD is not much different from those of catalyst-induced polymerizations. Therefore, the high reactivity of CPD in cationic polymerization (large k_2 values)

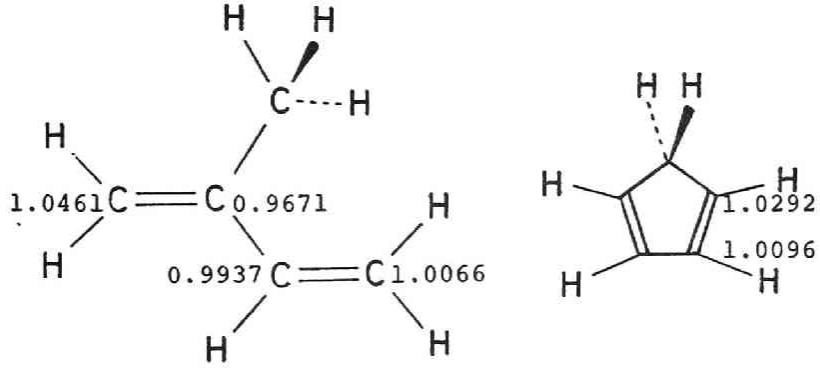
TABLE III

Activation Parameters of Propagation in the Vinyl Polymerization of Styrene, Isobutyl Vinyl Ether, and CPD

Monomer	Catalyst	Solvent	E_p Kcal/mole	log A_p	Reference
Styrene	BPO	bulk	7.8	7	13
"	Cs^+(ion pair)	THF	5.4	5.7	14
"	Cs^+(free ion)	"	5.9	9.1	"
"	I_2	$(CH_2Cl)_2$	6.0-6.5	1.3-2.1	4
"	radiation	bulk	2.2	8.0	5
Isobutyl Vinyl Ether	$C_7H_7{}^+SbCl_6{}^-$	CH_2Cl_2	6	4	9
"	radiation	bulk	9.6	12.1	10
CPD	$TiCl_4$-TCA	toluene	6.0	10	present thesis

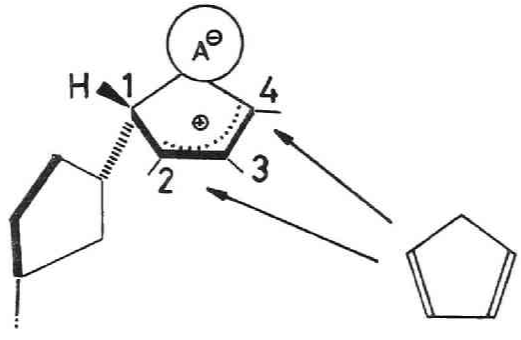
should be explained by the entropy term of the rate constant. It has been believed that free-radical, free-anionic, and free-cationic polymerizations show larger frequency factors than ion-pair polymerization. This is consistent with the proposal by Kanoh et al.[4] that the presence of counter ion in cationic polymerizations makes the motion of the growing end hindered, which lowers the frequency factor of the ion-pair propagation. The frequency factor of CPD polymerization, which is of paired-ion type, is in the region of the magnitude for free-ion polymerizations. In this connection CPD is again an exception.

To explore a possible explanation for this anomaly, the electronic densities of CPD and isoprene calculated by Yonezawa[15] according to the CNDO/2 method are indicated below:



The π Electron Density

carbons 1 and 2 (and necessarily carbons 3 and 4, too) in CPD have higher π electron density than the formal valency (1.0 for the π electron density). On the other hand, carbons 2 and 3 in isoprene have lower electron densities. Therefore, the electrophilic attack of a propagating cation is possible to take place at carbons 1, 2, 3, and 4 of CPD, whereas only at carbons 1 and 4 of isoprene. Furthermore, since the growing carbonium ion i.e. cyclopentenyl cation is very stable as noted in earlier chapters, the following model of the growing chain end seems to be justified as Aso and Ohara proposed.[16]



Because the cyclopentenyl cation is highly stabilized by the delocalization of the positive charge and the ion-pair is very loose as previously stated, the counter anion (A^-) is not located on the specified carbons but above the cyclopentenyl ring. So, CPD is possible to add both to 2 and 4 positions of the ion as indicated in the scheme. Thus the high frequency factor of CPD polymerization might be based on the multiple

modes of the propagation reaction.

This explanation is supported by the microstructure of polycyclopentadiene (PCPD). The nuclear magnetic resonance spectra of PCPD[17] indicate that the PCPD produced under the present conditions is composed of roughly equall amount of 1,2- and 1,4- structures regardless of the polymerization temperature. These experimental findings suggest the multiple modes of propagation reaction in the propagation of CPD.

It is interesting to note that, in the ring-opening cationic polymerization, cyclic monomers such as oxetanes showed a very high frequency factor and it was concluded that the activation entropy is more influential in the determination of the propagation rate of oxetanes.[18] The rate order of three oxetanes was accounted for on the basis of the difference of ease of desolvation in going from the solvated intitial state to the desolvated transition state, but the desolvation can not be considered to be the main reason for the large frequency factor of CPD, since the charge in cyclopentenyl cation is supposed to be much delocalized as shown previously.

To conclude, the present investigation showed that, in the polymerization of CPD, the growing ion-pair has a propagation rate constant larger than 10^4 l/mole/sec, which is comparable to that of free ions. This high reactivity of CPD in the cationic polymerization is shown to be due to the entropy term, i.e., high frequency factor, which could originate from the multiplicity of the mode of propagation reaction.

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SUMMARY

In this thesis, the chemistry of the cationic polymerization of cyclic dienes were studied mainly by means of kinetic method. The kinetic features of the polymerizations of four cyclic dienes, i.e. cyclopentadiene, methylcyclopentadiene, 1,3-cycloheptadiene, and 1,3-cycloöctadiene were elucidated in Part I and their reactivities were investigated by the copolymerization in Part II. In Part III, the propagation rate constants of cyclopentadiene were determined under various conditions and the factors responsible to the reactivity of this monomer were discussed.

The results will be summarized below.

PART I. POLYMERIZATION REACTION OF CYCLIC DIENES WITH CATIONIC CATALYSTS

Chapter 1. Cyclopentadiene

Section 1.1 Polymerization with Titanium Tetrachloride–Trichloroacetic Acid

Cyclopentadiene was polymerized in toluene by $TiCl_4$-CCl_3COOH at -78°C. The polymerization rate was extremely large at the initial stage, but the conversion-time curve soon levelled off,

when the unreacted monomers were still present. At a given catalyst concentration, the final conversion increased with decreasing the initial monomer concentration, and at a given monomer concentration, the final conversion increased with increasing concentration of either $TiCl_4$ or CCl_3COOH.

When monomer or CCl_3COOH was introduced into the "dormant" polymerization system, the conversion of monomer neither increased nor decreased. However, when $TiCl_4$ was added to the system, the polymerization was reinitiated. These experimental results indicate that the polymerization terminated as a result of the catalyst inactivation by monomers during the polymerization. By-products formed by $TiCl_4$ and monomer were confirmed by the spectroscopic measurement.

Section 1.2 Polymerization with Stannic Chloride-Trichloroacetic Acid and Boron Trifluoride Etherate

Cyclopentadiene was polymerized with $SnCl_4$-CCl_3COOH or $BF_3 \cdot O(C_2H_5)_2$ in toluene at -78°C. When $SnCl_4$-CCl_3COOH was used as a catalyst the polymerization was very rapid at the beginning but later it slowed down. The first-order plot with reference to the monomer concentration was curved for the early stage of the polymerization, so that the stationary concentration of active species was not established in this stage. However, the linearity of the first-order plot was established toward the end. From these results, it was considered that two different types of polymerization (stationary and non-stationary) occurred simultaneously in this system. Intrinsic viscosities of the

resultant polymers decreased with the increase of the catalyst concentration, which is characteristic of non-stationary state polymerization.

The polymerization induced by $BF_3 \cdot O(C_2H_5)_2$ was much slower than that by $SnCl_4$-CCl_3COOH, and the first-order plot of the polymerization was approximately linear except for the very beginning of the polymerization. Taking into account these findings as well as those found in the polymerization by $TiCl_4$-CCl_3COOH, a tentative mechanism was proposed for the initiation reaction of cyclopentadiene polymerization. The interactions among a monomer, a catalyst, and a cocatalyst were considered to determine the kinetic behaviour of the polymerization.

Chapter 2. Methylcyclopentadiene

Methylcyclopentadiene was polymerized with cationic catalyst in toluene solution at -78°C to a white powdery polymer, whose intrinsic viscosity in benzene solution at 30°C ranged from 0.1 to 0.5 according to the polymerization conditions. Comparison of the rate of polymerization suggested that methylcyclopentadiene was more reactive than cyclopentadiene. This was interpreted in terms of the electronic effect of methyl group and a high stability of cycloalkenyl cation. Infrared and NMR spectra of polymethylcyclopentadiene produced under the present conditions showed that the polymer had a trisubstituted double bond, i.e., the propagation reaction took place with a double bond not carrying a methyl group. Thus, the methyl group

of methylcyclopentadiene influenced the reactivity and the polymer structure.

Chapter 3. 1,3-Cycloheptadiene

1,3-Cycloheptadiene was synthesized and polymerized. It did not polymerize with radical initiators. It polymerized very slowly with anionic catalyst (n-Butyl Li). Ziegler–Natta type catalyst was moderately active. Cationic catalysts were the most effective, but the polymerization rate was much smaller than that of cyclopentadiene. The kinetic behaviour of the cationic polymerization of 1,3-cycloheptadiene was similar to those of other conjugated cyclic dienes, i.e. relatively fast polymerization at an initial stage and the rate rapidly slowed down toward the end.

The structure of the cationically obtained poly-1,3-cycloheptadiene was very complicated. It consisted of at least four different structures. The migration of hydrogen ion and the transannular polymerization must have occurred in the polymerization of 1,3-cycloheptadiene.

Chapter 4. 1,3-Cycloöctadiene

Cis,cis-1,3-cycloöctadiene was polymerized by $TiCl_4$-CCl_3COOH in methylene chloride or toluene at -78°C. When the polymerization was conducted in methylene chloride, the polymerization was fast only at the beginning and after that it stopped completely,

leaving unreacted monomers. On the other hand, when toluene was used as a solvent, a slow polymerization was observed after the fast polymerization, and the polymerization went to completion. The conversion reached during the fast polymerization was lower as the initial monomer concentration was higher. These experimental findings were interpreted in terms of a strong interaction between monomer and catalyst to form an inactive compound in methylene chloride. A reactivation of this compound might be possible in toluene to result in a slow polymerization.

The reactivities of cyclic dienes in the homopolymerization were found to be in the order : cyclopentadiene > 1,3-cyclohexadiene > 1,3-cycloheptadiene > 1,3-cyclooctadiene. Poly-1,3-cyclooctadiene obtained under the present conditions was of low molecular weight presumably on account of monomer-transfer reactions.

PART II. COPOLYMERIZATION STUDIES OF CYCLIC DIENES

Chapter 5. Cationic copolymerization of Cyclopentadiene with α-Methylstyrene

Cyclopentadiene was copolymerized with α-methylstyrene by a cationic catalyst and the monomer reactivity ratios were determined. Formation of the true copolymer was confirmed by the fractional precipitations of the product. Cyclopentadiene was more reactive than α-methylstyrene, and solvent polarity hardly affected the monomer reactivity ratios. It was deduced

from the pK_{BH}^+ values of cations pertinent to the present investigation that there is little difference between the stabilities of cyclopentenyl cation and cumyl cation. This could explain the absence of solvent effect on the monomer reactivity ratios, since the two sorts of ions would gain equal stabilization energy by solvation. The higher reactivity of cyclopentadiene therefore suggests that cyclopentadiene is more nucleophilic than α-methylstyrene.

Chapter 6. Copolymerization of Cyclopentadiene with 2-Chloroethyl Vinyl Ether and Some Properties of the Copolymer

Cationic copolymerizations of cyclopentadiene with 2-chloroethyl vinyl ether were carried out at -78°C using boron trifluoride etherate as a catalyst. Toluene, methylene chloride, and nitroethane were used as solvents. In each solvent the monomer reactivity ratios were determined and it was shown that cyclopentadiene was more reactive in methylene chloride and nitroethane but less reactive in toluene than 2-chloroethyl vinyl ether. This solvent effect on the relative reactivity of the monomers was interpreted on the basis of a higher nucleophilicity of cyclopentadiene than 2-chloroethyl vinyl ether and a lower stability of cyclopentenyl cation than the alkoxy substituted carbonium ion.

The copolymer was cured with sulfur. Some mechanical properties of the copolymer and their vulcanizates were investigated. The copolymer showed the properties as a useful elastomer.

Chapter 7. Copolymerization between Cyclic Dienes and Their Relative Reactivities

To investigate the influence of ring size on the reactivity of cyclic dienes, the relative reactivities of 5–8 membered cyclic dienes were studied by copolymerization. The reactivity of these cyclic dienes decreased in the order : methylcyclopentadiene > cyclopentadiene > 1,3-cyclohexadiene > 1,3-cycloheptadiene > 1,3-cycloöctadiene. This order of reactivity is same as the order of homopolymerization rate. Obviously the ring size influenced the reactivity. As a factor to determine the reactivity of cyclic dienes, the dihedral angle between the two double bonds was proposed. This angle directly influences the conjugation of dienes. A necessary conclusion is that the higher the conjugation, the more reactive the diene in cationic copolymerization. The high nucleophilicity of the monomer and the stability of the intermediate cation seemed to explain the high reactivity of cyclopentadiene. Contribution of these two factors to the reactivity of most vinyl monomers were discussed in particular reference to the solvent effect in the cationic copolymerization.

PART III. PROPAGATION RATE CONSTANTS IN THE CATIONIC POLYMERIZATION OF CYCLOPENTADIENE

Chapter 8. Polymerization with Titanium Tetrachloride-Trichloroacetic Acid

The propagation rate constant of the cationic polymerization of cyclopentadiene induced by $TiCl_4$-CCl_3COOH was determined in a toluene solution at -75°C. All manipulations were made using vacuum lines. Time-conversion curves were drawn by following the exothermicity of the fast reaction in an adiabatic system. The kinetic equations were developed to determine the propagation rate constant, which involved a fast initiation reaction and diminising concentrations of active species (non-stationary state kinetics). For the present system, the propagation rate constant was 350 l/mole/sec, which was larger than those so far reported for the cationic polymerization of some vinyl monomers in non-plar solvent. It was also demonstrated that the termination reaction was a pseudo-unimolecular reaction and the mechanism of the reaction was discussed.

The present method is applicable to a wide variety of conditions to determine the propagation rate constant, where a polymerization accompanied with a fast initiation reaction and some termination reactions takes place.

Chapter 9. Polymerization with Perchloric Acid and Acetyl Perchlorate Catalysts

Cyclopentadiene was polymerized with $HClO_4$ and with CH_3COClO_4

at -78°C. Toluene, methylene chloride, and their mixture were used as solvents. The kinetic features of the polymerization were similar to those with $TiCl_4$-CCl_3COOH except that the final yield was not dependent on the initial monomer concentration. The propagation rate constant k_2 were determined according to the kinetics proposed by Pepper, et al., for styrene-H_2SO_4 system. The values of k_2 by $HClO_4$ agreed with that by CH_3COClO_4, which was expected from the identity of the counter ion. It was also found that the propagation rate constant k_2 depended greatly on the counter ion; k_2 values for CH_3COClO_4 and $HClO_4$ were much smaller than k_2 for $TiCl_4$-CCl_3COOH. Furthermore, k_2 obtained in toluene was smaller than that in methylene chloride. All these difference in k_2 values are interpreted by the different influence of the anionic moieties in the propagating ion pairs.

Chapter 10. Activation Parameters for the Propagation Reaction of Cyclopentadiene by Titanium Tetrachloride-Trichloroacetic Acid

The propagation rate constant for the cyclopentadiene–$TiCl_4$-CCl_3COOH–toluene system was determined at different temperatures to estimate the activation energy E_p and the frequency factor A_p of the propagation step. The Arrhenius plot of the propagation rate constants determined at -20°C – -90°C gave

$$\log A_p = 10$$

$$E_p = 6.0 \quad \text{Kcal/mole.}$$

The activation energy is not much different from the values so

far reported in cationic polymerization of vinyl monomers. Therefore, the high reactivity of cyclopentadiene should be explained in terms of the activation entropy of the propagation reaction. In fact, the logarithm of A_p was very large for the paired-ion polymerizations and was in the range of values for free-ion polymerizations. This high frequency factor was tentatively interpreted assuming the multiplicity in the propagation mode of cyclopentadiene.

LIST OF PUBLICATIONS

Chapter 1

Section 1.1 Kobunshi Kagaku, 23, 119 (1966).

Section 1.2 J. Macromol. Sci.-Chem., A2, 471 (1968).

Chapter 2 J. Polymer Sci. Part A-1, 6, 809 (1968).

Chapter 3 To be published.

Chapter 4 J. Macromol. Sci.-Chem., A3, 237 (1969).

Chapter 5. J. Macromol. Sci.-Chem., A2, 1423 (1968).

Chapter 6 Angew. Makromol. Chem., 27, 189 (1972).

Chapter 7 To be published.

Chapter 8 J. Polymer Sci. Part A-1, 9, 747 (1971).

Chapter 9 Chemistry Lett., 1972, 671; ibid., 1973, 1007.

Chapter 10 To be published.

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